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Plenary

Pulse TA®, a promising extension of coupled TA devices and its contribution to the chemistry of fluorides

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Keywords: pulse thermal analysis, sol-gel-prepared fluorides, adsorption, desorption, gas-solid reactions

Pulse thermal analysis, PulseTA® (PTA), has been developed as a thermoanalytical technique more than 20 years ago by Maciejewski et al. [1]. Basically, it represents an extension of TA-MS coupling devices by a gas dosing unit. Permanent gases can be pulsed onto a solid thus allowing for studying its interaction with the sample. Qualitative evaluation is possible via monitoring the changes of the product gas composition. Quantitative evaluation of ion current (IC) or FT-IR signals after preceding calibration allowed for separating different contributions to a given TG step.

The great potential of PTA for contributing to solid state chemistry in general has been comprehensively reviewed [2]. The application field of PTA was expanded by the possibility of injecting evaporable liquids using self-made injectors, e.g. for MeOH to characterize the acidic and basic surface sites of sol-gel-prepared alkaline earth fluorides MF2 (M=Ca, Mg, Ba) and others [3]. Technically important reactions such as the formation of fluorination catalysts by an HF treatment at elevated temperatures could be simulated by PTA [4].

Various experimental approaches were applied for concluding on reactivities in both a qualitative and semi-quantitative way and, in certain cases, even on the discrimination between different reaction pathways:

(1) Alternating injections of different reactants for comparing the interaction's strength.

(2) Intermediate action of inhibiting substances (e.g. water) for clearing the question "Who blocks whom?"

(3) Adsorption/desorption studies (Fig. 1), sometimes including the determination of the surface coverage.

(4) How to perform a suitable blank experiment?

Recent work was focused on dehydrofluorination [5] and hydrodechlorination [6] reactions performed with nanoscopic aluminium chlorofluoride (ACF) as a catalyst. Binary solid-gas systems such as ACF(s)/benzene(g), ACF(s)/Et3GeH(g), ACF(s)/1-fluoropentane(g) or ACF(s)/dichloromethane(g) were investigated. As an example,

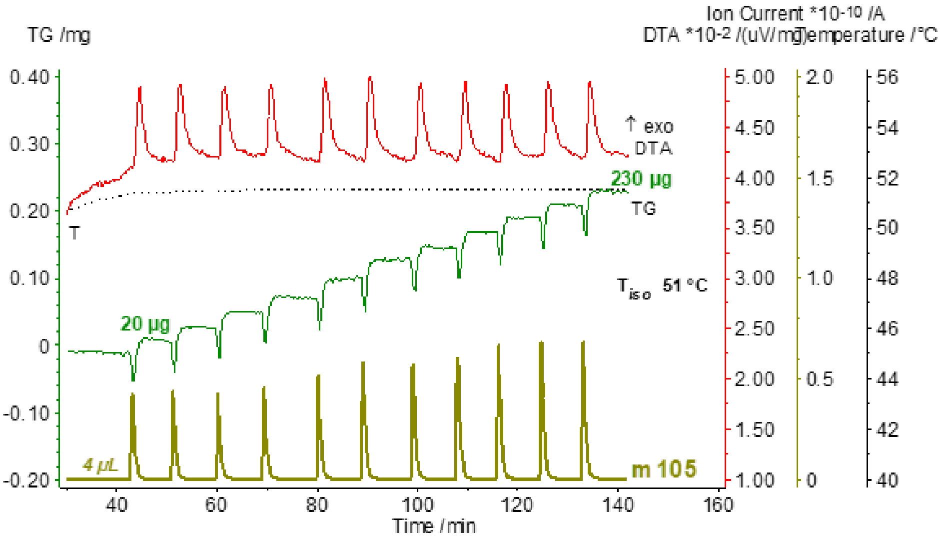

Figure 1. Isothermal PTA curves of a ther-mally pretreated (140°C) ACF (25.24 mg) in argon with the IC curve for the mass number m/z=105 (EtGeH$^+$) indicating the injected Et_3GeH. 11 pulses of 4 µL liquid germane which is immediately evaporated in the heated injector were injected. The curve course both of the exothermal DTA effects and the TG steps indicate pure chemisorption. Note that the sharp spikes in the TG curve preceding the mass gain steps represent buoyancy effects due to the high density of the injected Et_3GeH.

Figure 1 shows the interaction of gaseous Et3GeH with solid ACF – it can be interpreted in terms of a surface loading which obviously is not finished even after 11 injections.

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Utilization of aluminosilicate by-products in binding mixtures – benefits and limitations

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Keywords: aluminosilicate materials, hydration of cements, thermal analysis methods

In the world literature there is a tendency to study low-cement or no-clinker binders which can be considered as a more ecological and economic alternative for cement. Such binding mixtures can be prepared with the use of some aluminosilicate materials of natural or industrial origin (by-products).

Generally speaking, fine-grained aluminosilicates can be used in different quantities in binding compositions, from small or moderate amounts (admixtures, additives) to significant replacement of cement by aluminosilicate. It strictly depends on activity of the material, its physical properties (e.g. porosity) and required properties of final material. A lot of such materials do not contain sufficient amount of calcium components, thus they cannot exhibit self-cementing properties under the influence of water. However, in the presence of alkaline solution, they can form hardened structure depending on the kind of alkaline media, properties of aluminosilicate material and conditions of reaction (e.g. temperature). In contact with $Ca(OH)_2$ so-called pozzolanic reaction takes place.

Spent aluminosilicate catalyst from petrochemical industry may be an example of fine-grained, highly active pozzolanic material. Its proper use in Portland cement composites improves some properties of cement concrete, such as compressive strength [1]. This spent catalyst, used as a reactive additive, influences also hydration of calcium aluminate cements [2]. However, this material shows highly developed specific surface area, which reduces workability of the fresh mixture.

Fly ash is an example of pozzolanic material which different amounts can be used in binding mixtures. Typical amount of fly ash, commonly used, in cement composite does not exceed 35%. However, its higher content, i.e. about 55% (so-called high volume fly ash concrete) and even more, can also be considered [3,4]. Finally, hardened material produced entirely without cement (fly ash and an alkaline chemical activator only) can be created.

Thus, one can conclude that proper use of aluminosilicate materials can modify and enhance properties of cement composites. However, in the case of blends containing low amount of hydraulic component (cement) and high amount of pozzolanic material in the mixture an elongation of initial setting time, slowing of hardening and reduction of early compressive strength is often observed. Such blends may require activation, e.g. by Na2SO4 or by introducing small amount of high pozzolanic material [4,5]. Fine-grained spent aluminosilicate catalyst of high pozzolanic activity can be considered for this purpose [6].

The aim of this lecture is to discuss the role of selected aluminosilicate materials in different binding compositions, in the aspect of their utilization and development of the features of final materials, including their long-term properties. Some benefits but also limitations relating to such utilisation of aluminosilicate by-products are discussed. Usefulness of calorimetry and thermal analysis methods (very important techniques to investigate chemical processes taking place in binding mixtures) is presented.

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Thermal Analysis for combustion research: data interpretation and challenges

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Keywords: VOCs Emission; sorbent tube; TD-GC/MS; Online FTIR

The emission of volatile organic compounds (VOCs) during coal combustion at different heating rates in a power plant boiler, a drop tube furnace and a TGA reactor was studied. The results indicate that TG-FTIR-GC/MS with a slow heating rate is a good method to study the release of VOCs during coal pyrolysis. This technique produces sufficient amounts of VOCs, provides information about VOC formation as a function of time and the mechanism of VOC formation during coal pyrolysis. TGA uses a large amount of oxidant during combustion and VOCs in the exiting flow are low. Drop-tube furnaces are operated under laminar conditions. The VOCs near the centerline of the tubular flow have very short pyrolysis times, and they have high concentrations in the exiting flows. Turbulent flow in the power plant during combustion enhances the mixing of primary VOCs with oxidants and pushes the combustion towards completion. The majority of the VOCs identified in this study may not be observed in a large scale coal boiler. Thus, an intermediate heating rate device, such as a drop tube furnace, can be used to determine the effect of a fast heating rate on the formation of VOCs. This study demonstrated that the drop tube furnace results were similar to the results from a large-scale coal boiler. However, the information on the effect of air pollution control devices on the VOCs emission can only be obtained from power plant tests. Utilized together, results from the fixed bed reactor, drop tube furnace and boiler, provide a more complete VOC profile than one technique alone.

Acknowledgments

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Formulation, structural and thermal analysis of an innovative buccal mucoadhesive film drug delivery system from two different polymers

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Keywords: mucoadhesive buccal films, chitosan, sodium alginate, cetirizine, thermoanalytical characterization, TG/DSC, TG-MS

Background: Nowadays, mucoadhesive buccal films are in the foreground because they are easy to apply, and with this formulation we can avoid the first pass effect, which causes that a lower amount of active ingredient can reach the same effect and they have good patient compliance, too. Currently, the buccal administration of active ingredients by mucoadhesive films is one of the most innovative ways we can use to achieve systematic drug delivery.

The bases of buccal mucoadhesive preparations are polymers, which have mucoadhesive properties, such as chitosan, sodium alginate, hydroxypropylmethylcellulose (HPMC) or sodium hyaluronate. Plasticizer additives, for instance, glycerol or polyethylene-glycol can be used in the film to make the administration easier by increasing the elasticity of the preparations. Permeation enhancers are also used in buccal mucoadhesive films as additives to improve bioavailability (e.g.: EtOH).

Aim: We used chitosan (CH) based films, which can provide a small amount of active substance absorption through the buccal mucous membrane, thereby avoiding the hepatic first pass effect. We prepared oral mucoadhesive films from sodium alginate, too, in which we used 10 mg of cetirizine as active substance.

The films were prepared with the solvent casting method on Teflon surface. We examined the free volume of the films with positron annihilation lifetime spectroscopy (PALS). The Fourier transform infrared spectrometer (FTIR) spectra give us useful information about the structure of the films as well.

We also focused on determining the thermal characteristics of mucoadhesive films. The thermoanalytical examinations of the films were carried out with a Mettler Toledo TG/DSC1 instrument. During the measurements, the start temperature was 25 °C, the end temperature was 500 °C, and the applied heating rate was 10 °C min-1. Nitrogen atmosphere was used. The thermal characteristics of the sample mass loss were determined with TG coupled with a quadrupole mass spectrometer (ThermostarTM GSD 320).

We investigated the dissolution of the active substance from the polymer film as well.

Results and discussion: In case of chitosan (CH) based films we used ascorbic acid (AscA), which provides acidic pH and has permeation enhancer properties as well. We compared the AscA effects on the properties of films with films prepared with acetic acid (AA). The optimal AscA amount is the lower concentration when the dissolution is provided by the acidic pH, but it can still build into the structure of the films.

PALS shows us that the free volume increases and the higher amount of AscA cannot build into the structure of the films. This is also confirmed by the FTIR spectra. We detected the thermo-analytical curves of the main substances and the films, which give us further information about the structure, thermal stability and degradation.

The interactions seen in the case of the thermoanalytical properties of alginate based films are more pronounced between the components constituting the film than in the spectrum obtained by the FT-IR device at room temperature. However, as these processes occur at a much higher temperature, they do not affect the normal stability of the films.

The dissolution test shows that regardless of the concentration of polymer and glycerin, the total amount of the active ingredient is dissolved, with no significant differences in dissolution rates and profiles.

Invited

Studying reversible reactions and chemorheological behaviour for the additive manufacturing of self-healing actuators

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Over the past decade, the development of self-healing or remendable polymers markedly increased. Our work in this field is focussed on thermoreversible polymer networks based on the thermoreversible Diels-Alder reaction between furan (diene) and maleimide (dienophile) groups. Detailed knowledge about the reversible reaction kinetics and the connected chemorheological changes, gained through extensive use of thermal analysis and dynamic rheometry, helped us to develop these materials and their processing for application in self-healing (SH) soft robotic actuators [1–3].

The principle of these materials is quite straightforward: at high temperatures, the Diels-Alder/retro Diels-Alder reaction equilibrium is shifted towards the disconnected state, while at low temperatures, the cycloadducts are formed through the Diels-Alder reaction, linking the network together. A complicating factor is the existence of two stereoisomeric cycloadducts: one being more thermodynamically stable, while the other one forms faster [4]. As the network formation occurs at a lower temperature, e.g., in ambient conditions, it is generally quite slow, so the knowledge of the thermoreversible reaction kinetics is crucially important for optimizing the temperature program used during processing or healing. Moreover, combining this kinetic information with detailed insight in the conversion and temperature dependent visco-elastic behaviour of the materials facilitated the adaptation of the network composition to tune the material behaviour during processing and healing.

A comprehensive study of the thermoreversible reaction kinetics, using DSC, microcalorimetry, and FTIR and NMR spectroscopy, provided a reaction kinetics model that can be used to simulate the changes in the cross-linking of the polymer network upon heating and cooling, facilitating the optimization of temperature schedules for a specific material, as well as the optimization of the network composition to ease the processing or improve the healing kinetics.

The reversible gel conversion, the reaction conversion at which the material switches between a liquid and elastic state (and vice versa), is crucial for the design of healing protocols, during which the shape of the object must be retained. Of course, the chemorheology can be tuned by a careful selection of the building blocks used to construct the network, which was a key aspect for the development of filament extrusion and filament deposition modelling of these thermoreversible polymer networks [3,5].

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Self-nucleation and heterogeneous nucleation of polypropylene micro-droplets in immiscible blends

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Keywords: polymer crystallization, nucleation, polypropylene, immiscible blends, nucleating agents

Nucleating agents are common polymer additives, widely used for speeding up processing and tune the final mechanical properties. Despite their industrial importance, the scouting of different substances in search of highly efficient nucleant is still mainly empirical. A convenient efficiency scale has been defined by comparing the increase in non-isothermal crystallization temperature of a nucleated sample with respect to the neat polymer, with the one obtained by self-nucleating the same material at an optimal melting temperature. [1] However, also due to the combined effect of the nucleation and growth process in determining the crystallization behavior of bulk samples, the so-derived efficiency scale remains an useful, but empirical, evaluation. Ideally, one would need to probe the sole effect of the nucleation step, and compare the different substances on the basis of the free energy barrier for the formation of a critical nucleus on their surfaces.

When crystallizable polymers are confined into isolated micro or nanodomains, e.g. in immiscible blends or block-copolymers, nucleation turns out to be the rate determining step in the overall crystallization, which displays a first order kinetics. [2] In this work, the nucleation process of polypropylene droplets dispersed in a polystyrene matrix and containing various nucleating agents (i.e., sodium benzoate, NA11, and quinacridonequinone), has been investigated by stepwise crystallization and melting with Differential Scanning Calorimetry (DSC). Moreover, self-nucleation of neat i-PP droplets was also studied, revealing that crystal growth via secondary nucleation is the rate-determining step of the crystallization process. Therefore, the nucleating efficiency of the various heterogeneous nucleating agents could be quantitatively compared on the basis of the derived free energy barrier for critical nucleus formation, ΔG^*. Finally, the empirical efficiency scale of heterogeneous nucleants was successfully correlated with the ratio of ΔG^* between secondary nucleation (self-nucleation) and nucleation on a given substance.

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Thermal analysis study of vaporization of ionic compounds. The case of tetramethylammonium iodide

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Keywords: ionic liquids, vaporization, decomposition, dissociation, tetramethylammonium iodide

Thermal analysis, with particular reference to thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are irreplaceable tools, although the usual complexity of the processes that a solid or a liquid undergoes, needs the use of complementary techniques (the most common being FTIR, XRD, SEM) to support the interpretation of thermal analysis results.

One of the more rapidly growing areas of chemistry research involves room-temperature ionic liquids and low-melting ionic solids, due to the wide range of possible cation and anion combinations that allows for a large variety of tunable interactions and applications. As far as the most important property of the former is concerned, the low volatility attracted interest in the last decade, due to the possibility to measure their even low vapor pressures at temperatures lower than those where decomposition takes place. However, the risk that vaporization and thermal degradation may occur simultaneously cannot be excluded. Several examples will be presented in which the vaporization and thermal degradation of some imidazolium ionic liquids have been investigated by using a multitechnique approach that combines TG-DTA with two conventional Knudsen Effusion methods: i) Knudsen Effusion Mass Loss (KEML) and ii) Knudsen Effusion Mass Spectrometry (KEMS) [1].

The thermal decomposition of alkylammonium lead halides, belonging to the class of perovskites currently considered with great expectations as possible light harvesting materials for photovoltaic devices, has been recently studied [2]. Before these materials could be considered for such applications the stability of alkylammonium lead perovskites should be improved by replacing the halide anion or the tetravalent cation (i.e., lead by antimony) [3]. To have a clear understanding of the processes occurring with increasing the temperature a simpler prototype must be selected, and its thermal decomposition studied in detail.

To this end, the case study that I will present concerns the thermal behavior of tetramethylammonium iodide, $(CH_3)_4NI$ (TMAI), by means of simultaneous TG-DTA experiments under inert (Ar) atmosphere up to 500°C. A single step of mass loss is evidenced between 300 and 450°C, accompanied by an endothermic effect. The reaction mechanism is described in the light of the gases evolved upon heating in the suitable temperature range according to the analysis of MS spectra (provided by the coupled TG-MS apparatus). In order to complete this investigation a kinetic study of the thermal decomposition has been carried out using two different isoconversional methods [4,5]. The conversion dependence of activation energy derived by both methods will be presented and the results compared.

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Application of nanofluids in renewable energy

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Keywords: Nanofluids, Renewable Energy, Challenges, Applications

It has been more than two decades from the discovery of nanofluids – mixtures of common liquids and solid nanoparticles less than 100 nm in size. Nanofluids have become a hot research topic in the fields of thermofluids due to their bespoke thermal properties. There have been numerous studies of nanofluids in recent years. Here, the latest developments on the applications of nanofluids in various renewable energy systems are presented. The effect of adding nanoparticles on the performance of renewable energy systems is discussed. The main energy systems include solar collectors, solar stills, and photovoltaic systems. Moreover, the environmental aspects of using nanofluids such as its effect on emission reductions are investigated.

Thermodynamic performance of a direct expansion solar assisted heat pumps using packed bed evaporator-collector

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Keywords: Solar assisted heat pumps, packed bed evaporator-collectors, thermal performance

The volumetric efficiency of compressor used in solar assisted heat pump systems is reduced due to the effect of superheating during peak sunshine hours. The loss of compressor volumetric efficiency has affects the heating capacity and coefficient of performance of a heat pump. To overcome this drawback, an attempt has been made in this research work to explore the possibility of using packed bed evaporator-collector to harvest the solar energy effectively during peak sunshine hours and maintain the superheat within 6 ^{o}C. The excesses solar energy harvested during peak sunshine hours has stored in the evaporator-collector using composite phase change material (composed of paraffin wax and grapheme). The experimental observations have been made during the year 2018 at Coimbatore climatic conditions in India. The standard energy performance parameters of direct expansion solar assisted heat pump (such as, condenser heating capacity, compressor power consumption, coefficient of performance and solar energy input ratio) and exergy performance parameters (such as, exergy destruction and exergy efficiency of compressor, condenser, expansion valve, collector evaporator and for the system) were evaluated. The results showed that, the condenser heating capacity, compressor power consumption and solar energy input ratio were significantly improved by using packed bed evaporator-collector. The energy losses in the evaporator-collector were significantly reduced by absorbing the heat using phase change materials packed in the evaporator-collector. Moreover, the packed bed evaporator-collector will deliver higher heat output in the condenser during off sunshine hours and also during fluctuations in sunshine hours.

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Kinetic of thermal decomposition of light and heavy crude oils by thermal analysis

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Keywords: crude oil, thermal analysis, kinetic

According to some agencies petroleum market reached values over more than One trillion of U.S. Dollars in 2018. Crude oil represented 50% of primary energy consumption at the beginning of this decade. For each reservoir existent of conventional petroleum or gas there is three times the amount of heavy crude oil in the planet. The International Energy Agency estimates that the reserves of unconventional oil and bitumen are about six trillion barrels worldwide, the equivalent of three times the amount of the reservoir of conventional oil and natural gas. The search for self-sufficiency in different countries in the crude oil industry has led to increased efficiency and investment in exploration, production, transportation, and refining. There is an urgent need to improve integration of actions and technologies, ranging from the outflow of oil in the tank, transport to the refinery, and ultimately the treatment and refining. One of the difficulties in handling petroleum, especially for heavy oils is processing, since the knowledge of its thermal behavior is not well understood. The present work investigated the thermal behavior of crude oils from Brazilian basins four samples with different °API values (27, 17, 13 and 11) by simultaneous thermogravimetry – differential scanning calorimetry – fourier transform infrared spectroscopy (TG–DSC–FTIR), and have established the kinetic parameters, and mathematical models associated with thermal decomposition process using Friedman and Ozawa-Flynn-Wall methods. Using the simultaneous technique TG/FTIR, it was identified relevant differences regarding sample 2 (17°API) and sample 4 (11°API) as the analysis were performed in both atmospheres, nitrogen and synthetic air. OFW analysis showed for the two samples of crude oil, with higher API values (27 and 17°API), that the values for each heating rate were located together within the isoconversional zone indicating that the model fitted the experiment well. Kinetic studies by Friedman and OFW showed that the sample 2 (17°API) had the highest values of activation energy, up to 60% conversion.

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Approaches for better thermal analysis – activities of the standardization working group of JSCTA (Japan Society Of Calorimetry And Thermal Analysis)

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Keywords: standard reference materials, education, DSC, TMA, RRT

The Working Group (WG) on Standardization of Japan Society of Calorimetry and Thermal Analysis (JSCTA) was established on 1999, and coined problems on the standardization of thermal analysis in the 31st Workshop held in 2000. Since then, challenges for solving two problems on standardization have been made; one is related to the certified reference materials, and the other concerns methodology. In 2003, the WG focused on the calibration of differential scanning calorimeters (DSCs), particularly the temperature calibration, and in order to realize the present status, enquiries were made to thermal analysis specialists and to the general users of thermoanalytical instruments. Furthermore, pure In, Sn, Pb, and Zn were prepared and put to round robin test (RRT) for evaluation as calibration standards. As a result, problems related on the user knowledge on instrument calibration, poor availability of the reference materials, cost and time-consuming calibration, uncertain calibration procedure, etc. have been realized. In 2005, based on the results, introductory practice course for understanding the importance of instrument calibration was incorporated for the first time in the three-day training short course. Since then, basic course for the beginners is held every year.

During 2007–2008, RRTs on the validation of cyclohexane as a reference material for the calibration of DSC, and of silicon single crystal and glass-like carbon (GLC) as a reference for measuring thermomechanical properties were carried out. These efforts resulted on the establishment of 3 certified reference materials (CRM) now available from National Metrology Institute of Japan (NMIJ) (Table 1).

The objective of this paper is to report and discuss on the challenges and the recent activities of Working Group (WG) on Standardization of JSCTA.

Table 1 Reference materials now available from NMIJ

Thermal Properties	Reference Material
Thermal Expansion	Silicon Single Crystal: 1101-a, 5803-a
	Glass-like Carbon: 1102-a, 1104-a
Specific Heat Capacity (low temperature)	Silicon Single Crystal: 5806-a
Phase transition	Cyclohexane for thermal analysis: 5401-a

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Use of calorimetry and thermal analysis to assess the mutual influence of cement and SCM during the hydration of composite cementitious binders

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Keywords: SCM, hydration, heat flow, pozzolanic heat, kinetics, mechanism

The hydration of pure cement was widely studied through different methods to determine the chemical reactions and their kinetics, mechanisms and thermodynamic equilibrium. It is undoubtedly established that hydration of OPC runs via a sequence of chemical reaction between different minerals of cement (C_3S, C_2S, C_3A, and C_4AF) and water to form gelatinous or semi crystalline calcium silicate hydrate denoted C–S–H, calcium sulfo-aluminate hydrate (ettringite- ($Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$) or monosulphate-$Ca_4[Al(OH)_6]_2(SO_4) \cdot 6H_2O$) and calcium hydroxide (CH) [1]. Apart from water that remains the fundamental cause initiating the hydration of cements; temperature, fineness, mineralogical and chemical composition of cements are among the key factors that influence the course of hydration reactions [2]. Nowadays, Supplementary cementitious Materials (SCM) are intensively used in combination with OPC in development of special construction materials such as Self-Compacting Concrete, High performance Concrete, Massive concrete and also in ordinary concrete by reducing hydration heat and shrinkage, by refining pore structure enhancing thus the durability of construction materials. SCM are divided into three groups. The first one is composed of natural or artificial pozzolanic materials among those metakaolin (MK) and pulverized fly ash (PFA) are mostly used. The second group contains latent hydraulic materials such as ground granulated furnace slag (GGBS), silica fume (SF). The last group is composed of nearly inert materials which interact weakly with cement matrix, but contribute to refinement of pore structure. The SCM belonging to the two first groups undertake through pozzolanic or alkali activation the reactions with calcium hydroxide released during the hydration of Portland cement (PC) to form additional hydrated products. Many references [2-3] reported pozzolanic or alkali activated reactions as due to the presence of calcium hydroxide. Much of them are satisfied with the comparison of hydration heat evolved by blended cement with reference one and express it in form of decrease of hydration heat mainly at short time. However few papers deals with the reciprocal influence of SCM on OPC hydration and with the determination of heat due to pozzolanic and alkali activated reaction. The present study is undertaken to quantify the heat of the pozzolanic or alkali activated reaction in hydrating systems with SCM and to characterize their mutual influence during the formation of CSH and ettringite by means of conduction calorimeter. Also, the work elucidates the mechanism and kinetics of reactions using data from calorimetric measurement and thermal analysis.

Heat evolution and the total heat evolved during the hydration were recorded using the 8-Channel TAM AIR isothermal calorimeter. Simultaneous thermogravimetric and differential thermal analysis (TGA/DSC – 1, STARe software 9.30, Mettler Toledo was used to identify and quantify different products. X-ray diffractometer Empyrean equipped with 2D fast detector and Cu-anode was used also.

Acknowledgements

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Do we know what the temperature is: from Newton's cooling law to a wider understanding of thermal analysis

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A temperature is a numerical measure of hot and cold. Its measurement is done by detection assuming the bulk behavior of a thermometric material. The fundamental physical definition of temperature is provided by thermodynamics and related to thermal equilibrium, i.e., no interrelated heat flow. Thermophysical measurements are historically outlined through the cases of differential thermal examinations (revealed from Rudberg 1820s to Russian Kurnakov 1940s) accentuating its impact to solid-state processes and application to both the fingerprinting, qualitative, quantitative and kinetic studies. The premature and still current DTA peak analysis seems to habitually copy the straightforward patterns of XRD analysis even if some specific aspects of heat measurements are principally divergent thus obviously focused to following discussion: such as the impact of heat transfer sluggishness affecting the DTA peak background (i.e. thermal inertia known since the Newton cooling law), associated creation of temperature gradients (particularly critical when using the extreme heating/cooling rates) and impact of the size of sample (the extent of its surface). The complexity of a DTA peak is explored in more details including necessary corrections due to both the sample thermal inertia and temperature gradients. The mathematical correction can be portrayed using the both differential (Tian) and/or integral (Newton) modes and confirmed by the effective rectification applied to DTA (and heat-flux DSC) responses reflecting well the need of heat inertia corrections as to attain the original shape of inserted rectangular heat pulse. Moreover during all extraordinary fast temperature changes arises a question whether the numerical values detected by a gadget really sustain the meaning of a real sample temperature and how to ever calibrate temperature under such extreme changes when is a high danger of deep undercooling/overheating (and disturbing effect of metastability). Besides a threshold of such a cooperative measurements can be exposed under rapid changes revealing thus a ceiling similar to a well-known Heisenberg quantum limit preventing a detached detection of a particle motion (~heat) from its position (~temperature). Relativistic understanding of temperature in remote sensing is discussed. Faulty applications when studying reaction kinetics are also discussed (especially critiquing the Kissinger evolution method).

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Thermal stability analysis of benzotriazole as an additive in lithium-ion batteries

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Keywords: lithium-ion battery (LIBs), electrolyte, benzotriazole (BzTz), differential scanning calorimetry (DSC), vent sizing package 2 (VSP2)

Lithium-ion batteries (LIBs) have been a crucial carrier for energy storage. However, the chemical reaction process of LIB is a major point of safety because the process may generate heat and pressure. Forced by high temperature, high pressure vapor may be generated by the electrolyte. Once the pressure is greater than the limitation, pressure ejection and heat release will occur with a severe explosion. This study focuses on the thermal stability of organic solvent, electrolyte with and without specific additive. We used lithium hexafluorophosphate (LiPF6) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as our lithium salts; then the organic solvent was composed of ethylene carbonate (EC), propylene carbonate (PC), and di-methylene carbonate (DMC) with volume ratio as 1:1:1. The benzotriazole (BzTz) was added into the electrolyte with different mass% as the additive. Temperature and pressure rise of electrolyte can be detected via differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). The oxidation process of the electrode was restrained from the BzTz, and the electrolyte reduced gas generation effectively. On the other hand, the pressure under high temperature was inhibited by the addition of additive in the study.

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Enhanced hydrogen storage by doping catalysts and nanoconfinement and thermal analysis study

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Keywords: hydrogen storage, nanoconfinement, thermal analysis

Energy and environment protection research have attracted many researchers' attention. Studies of economic, highly efficient and safe hydrogen storage materials (HSMs) are of great importance in the fuel cells based vehicles [1-3].

In our lab., studies on HSMs based one micro/nano-technology etc. were performed. The promising nano materials for HSMs such as MHx: M= Mg, La, Ni, etc., alanate, borohydride and MOF were conducted in out lab...By growth nanosized Cu-BTC on the surface of graphene, the GO/Cu-BTC composite shows enhanced hydrogen storage and CO_2 capture performance [2]. By doping graphene with polyaniline and Pd nanoparticles, the resulting Pd–PANI–rGO nanocomposite was highly sensitive and selective to hydrogen gas, with fast response time in air at room temperature. Both catalysts and nanoconfinement are favourable for improvement of thermodynamic and kinetic performance.

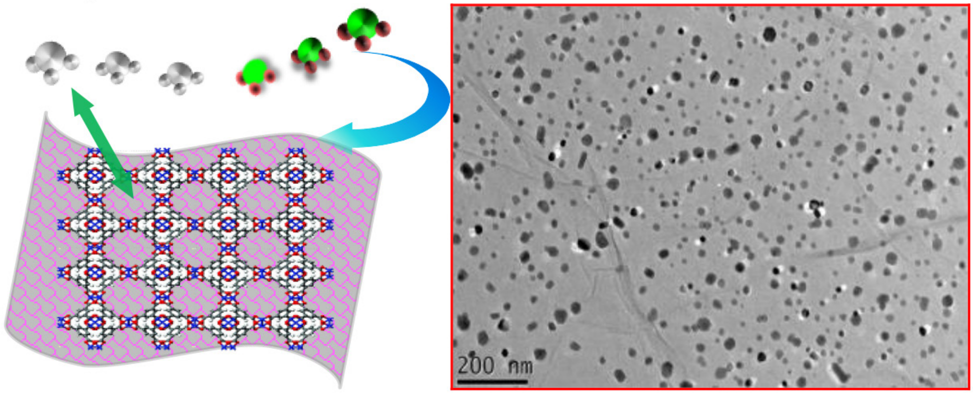

Figure 1 Graphene oxide induced nanosized Cu-BTC for gas adsorption.

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Thermal analysis of magnetic materials

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Keywords: thermal analysis, magnetic materials, magnetic shape memory, ferromagnetic.

Thermal analysis techniques (differential scanning calorimetry, thermogravimetry, dilatometry, thermomechanical amalysis, dynamic mechanical analysis) have multiple applications in the characterization of magnetic materials. On the one hand, they have been used to determine the characteristic temperatures of the magnetic transitions (Curie, Neel) and/or of the structural transformations (crystallization, austenite/mrtensite) that involve a change in the magnetic response of the material. On the other hand, they have been used to thermodynamically parameterize these materials (entropic and enthalpic calculations, activation energy, phase diagrams).

In particular, Fe or Co-based ferromagnetic alloys are characterized by their applications in high and low frequency devices. In this work, amorphous and nanocrystalline samples obtained in the shape of powder (by mechanical alloying) or ribbon (melt spinning) are analyzed. Microstructural parameters such as the crystalline grain size or the microstrain index determine the functional response (basically magnetic) of these alloys to a large extent [1]. A suitable heat treatment facilitates obtaining the desired properties (such as low coercivity and high saturation magnetization if the material has to be magnetically soft).

Another field of applications is that of shape memory magnetic materials (MSM) due to the magnetocaloric effect; with applications such as sensors, actuators or in magnetic refrigeration systems. These materials are characterized by having a magnetic transformation. MSM type Heusler alloys are also characterized by a martensitic transformation [2]. In his study, phase diagrams (based on experimental data) are constructed, which facilitate the prediction of those compositions that are candidates to present a high magnetocaloric effect in the working temperature range.

Likewise, some nanoparticulate alloys (based on lanthanides) that can present both the magnetocaloric effect and a correct capacity to store hydrogen will also be analyzed.

Evidently, in the study of magnetic materials, thermal analysis techniques must be complemented with techniques of structural analysis and magnetic analysis.

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Thermal analysis of coordination compounds with biological activity

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Keywords: coordination complexes, polymorphs, solvates, TG/DSC – MS, thermal stability – activity relationships

Coordination compounds have essential functions in living organisms. One can say that without coordination complexes there is no life despite the fact that the amount of metal-containing compounds is much lower than that of the organic ones. Therefore intensive research is taking place to synthesize new complexes with tailored biological functions.

Since the practical applicability of new compounds and materials, among others, depends on their thermal stability, the number of papers dealing with the thermal analysis of coordination compounds shows a constant increase. The aim of this presentation is to show how the thermoanalytical data can be exploited for a more detailed characterization of new compounds with specific biological activity.

The biological activity of a compound depends not only on the composition but on its crystal form. On the other hand, the crystal form of the compounds is highly dependent on the experimental conditions applied during the synthetic procedure. For rapid detection of the polymorphs is DSC the most frequently used experimental technique. As most of the reactions are carried out in solutions with different solvents, the compounds usually crystallize in the form of solvates with sometimes very different stability. The solvates are easily detected by thermogravimetry. In addition, during the storage, the exchange of the solvent for water may take place due to the humidity of air. For the determination of the type of solvent in coordination compounds, the use of combined techniques like TGA-MS or TGA-FTIR is very convenient. The amount of solvent can be calculated using the TGA data. The TGA data are suitable for the determination of the drying conditions, too.

Understanding the mechanism of decomposition of compounds with known crystal and molecular structure offers a better insight into the relationships between the structure and thermal decomposition pattern. Data derived from the joined studies of the structure determination, the physicochemical properties and biological activity of new compounds completed by quantum chemical calculations and calculations of the parameters used for the prediction of drug-likeness in comparison with the thermal analysis data reveals correlations between seemingly not related properties which are not yet explored.

Discuss of some flammability parameters derived from MCC Tests

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Keywords: microscale combustion calorimetry, heat release rate, flammability, derived parameters

Microscale Combustion Calorimetry (MCC) has been developed nearly 20 years, which is D7907, and regarded as a powerful facility to evaluate flammability. Several parameters, such as ignition capacity, heat release capacity, flame spread, fire growth rate, and fire resistance capacity characterizing flammability of materials can be derived from MCC. To study the reliability and uncertainty of these derived parameters, four materials were chosen and 108 samples tested by MCC with 9 heating rates. 5 parameters related to flammability of these materials are derived from test results, algorithms are compared. From the analysis, the robustness and practicability of the parameters and algorithms are evaluated, and new parameters are developed.

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Thermal behavior of gels obtained by microwave-assisted sol–gel

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Keywords: oxide nanostructures, microwaves assisted sol-gel method, thermal properties

The sol-gel method is a well-known synthesis procedure that allows a homogeneous distribution of all components at the molecular level and chemical bond formation between reagents in solution during the gelling process for polycomponent systems. The method is highly used for oxide nanostructure preparation. Lately, the investigation of the sol-gel synthesis in the presence of the microwaves (MW) has started to be of interest. The microwave assisted sol-gel method is most frequently used for obtaining nanocrystalline, monodispersed oxide nanoparticles or to transform amorphous gels into well crystallized nanopowders. Less studied was the influence of the microwaves on the sol-gel reaction in solutions. Some preliminary results on the influence of the microwaves on the sol-gel process and on the properties of the resulted nanostructures (films or powders) were published previously [1,2]. The first benefit of using MW assisted sol-gel preparation is the substantially increased stability of the resulted solutions against gelation, result that is of great interest for multilayer films deposition. The thermal investigations were realized on the samples used for films deposition and gelified at room temperature, using TG/DTA-MS method. The structural investigations of the thermally treated samples were realized by XRD measurements. A significantly higher thermal and more complex and prolonged decomposition were observed for the gels obtained in the presence of microwaves, especially for polycomponent systems. The results were correlated to the presence of a higher number and more complex molecular species in the resulted gels. Studies to establish the molecular species formed during the sol-gel process in the presence and absence of the microwaves are underway, in order to better explain the above-mentioned differences in the thermal behavior, structure and properties of the studied oxide nanostructures.

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Thermal analysis of intercalation phenomena in promising photocatalysts

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Keywords: perovskite-type titanates, organic-inorganic hybrids, photocatalysts, hydrogen production, intercalation, thermal analysis

Layered perovskite-type oxides are known as promising photocatalysts for hydrogen production by water splitting using sunlight energy. It has been shown that interaction with water leads to processes which can influence the properties of oxides: intercalation of water into the interlayer space and ion exchange of alkali cations to protons are typically observed for layered perovskite-like titanates and result in the photocatalytic activity [1].

New way to increase the photocatalytic activity of layered titanates is to use hybrid organic-inorganic perovskite type compounds. They present the promising class of materials for electronics, chemical technology, environment due to the combination of organic and inorganic properties within the molecular scale. Recent developments in the preparation of inorganic–organic hybrid materials from layered compounds focus on the intercalation or grafting reactions [2].

Thermal analysis is the effective way to investigate the intercalation phenomena of water and organic compounds in layered structure of materials. Thermochemical investigation is powerful not only from point of view of thermal stability but to determine the content of intercalates and to reveal the nature of bonding of inserting molecules with crystal structure as well [3].

Herein it will be reported results of thermal stability of organic-inorganic materials based on protonated forms of perovskite type layered titanates HLaTiO4 and H2La2Ti3O10 (Ln = La, Nd) belonging to Ruddlesden-Popper phases with different thickness of perovskite blocks. Objects under investigation are crystalline complex oxides intercalated by methylamine, butylamine, methanol. ethanolamine.

Simultaneous thermal analysis (TG+DSC) coupled with mass-spectrometry (MS) for gas evolution, FTIR-spectroscopy, powder XRD, SEM were used for the characterization of synthesized hybrids and investigation of process of their thermosdegradation. Advantages of TG coupled with MS for the quantitative analysis of the content of new hybrid organic-inorganic perovskite type compounds will be considered in comparison with XPS and CHN-analysis.

As items for the discussion will be the content of organic and water molecule intercalated in the interlayered space of layered structure, the evolution of cell parameters and distances between perovskite blocks accompanied the formation of hybrids, possibility of grafting with formation of covalent binding, the relative thermal stability of organic-inorganic compounds depending on the type of structure, the nature of rare-earth atoms, the type and size of the organic intercalate.

Results of the investigation of photocatalytic hydrogen evolution from different solutions and significant increasing in photocatalytic efficiency of hybrids will be presented.

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Sponsored Speakers

Innovations in Thermal Analysis – The new Flash DSC 2+

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Keywords: Innovations, Flash DSC 2+, STARe-software

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Thermal analysis STAR^e-software provides unrivalled flexibility and unlimited evaluation possibilities for example with the reference library, quality control or data integrity software options. The reference library option allows to organize and store any type of sample information in a centralized location and three different search functions to identfy thermal analysis data. Using the quality control option, it is possible to create a statistic template, perform a statistic evaluation and make a trend analysis. The latest software option data integrity allows to easily organize data for different users and define user rights.

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Solid-solid phase transition or melting peak: DSC with Microscope Accessory will let you know

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DSC thermograms can sometimes be complicated and difficult to interpret. On occasion, multiple DSC experiments must be performed to better understand a thermal event. The Discovery DSC Microscope Accessory allows you to view the sample while performing a DSC experiment. Microscope camera accessory make it easy to identify an endothermic solid-solid phase transition that may erroneously be interpreted as a melting endotherm. Also observe physical changes in a material as it undergoes phase transitions and volumetric dimensional changes, such as shrinkage associated with a transition, evaporation, or sublimation. The Discovery DSC Microscope Accessory is a high resolution digital microscope camera which simultaneously captures images and video during a DSC experiment. It has a temperature range of –180 °C to 725 °C and is compatible with the all our cooling systems.

The Discovery DSC delivers premium performance with advanced options and configuration flexibility intended to meet the requirements of the most demanding applications. Differential Scanning Calorimetry (DSC) measures endothermic and exothermic processes in materials and is widely used to characterize a broad range of materials to measure specific heat capacity, phase transitions, cure reactions, onset of oxidation, and heats of transitions (enthalpy). The Discovery DSC can be outfitted with accessories that enable scientists and engineers to get the most out of their data and their instrument investment. The Photocalorimeter is used to study UV cure reactions and the Discovery DSC Microscope Camera makes its easier than ever to view the sample while being tested.

Oral Presentations

Bio sciences, including food, soil, textile, wood

Thermal expansion of rib cartilage implants under Peltier cooling and laser heating

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Keywords: Cartilage, deformation, thermal expansion coefficient, autotransplantation, laser heating of biological tissue

Cartilage is excellent tissue for graft placement. The transplant can be the patient's own cartilaginous tissue or donor tissue stored in special donor cans at a temperature well below the temperature of the human body [1, 2]. When implanted, the cartilaginous tissue undergoes thermal expansion, resulting in a change in the size of the implant. The control of implant sizes is necessary when planning an operation for plastic surgery and laser reshaping of cartilaginous tissue [3]. Rapid cooling and thawing of ice in the tissue implants using a Peltier cooler and laser heating proceed in non-isothermal conditions. Therefore, the study of the thermomechanical properties of cartilaginous tissue under conditions of a high-temperature gradient, with different rates of cooling and heating, is of practical interest. The purpose of this work is to study the thermal expansion under Peltier cooling and laser heating of the samples of costal cartilaginous tissue isolated from the pig's rib, as well as to determine its thermodynamic characteristics: the specific heat capacity, the enthalpy of the interstitial water phase transition to ice, and the thermal expansion coefficient upon cooling and heating.

Selected rib cartilage samples of the pigs freezing bellow 0°C and heating up to +40°C were carried out with a Peltier thermoelectric cooler TEC1-12705 and Er-fiber laser "SCALPEL LASER LS-1.56" (IRE-Polyus, Russia). Non-isothermal kinetics of phase transition of interstitial water in cartilage to ice was observed using thermal vision system TESTO 845-1. Image acquisition and processing allow calculating thermal expansion coefficient (TEC) in dependence on temperature.

It is revealed that thermal expansion of the cartilage is influenced by the anisotropy of the internal structure of the tissue. Samples of rib cartilage, cut along the fibre bundle, are deformed 4 times stronger in length than in width. Either, the anisotropy of the cartilaginous tissue structure affects the rate of heating of the samples at the different conditions of heat transfer. Thus, the samples cut from the rib in two different ways, along or across the fibre bundle, have different heating rates and the duration of the phase transition. Laser heating rate of frozen samples cut across the fibre bundle 20% higher than along cut. Duration of ice melting for both types of the samples differs for 25%.

Acknowledgments

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The influence of pyrolytic conditions on Physico-chemical properties of animal bone char

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Keywords: animal bone char, IR spectroscopy, SEM/EDS analysis, thermal analysis, XRD

The lack of sustainable development is one of the key problems of many modern agricultural systems. Present-day farming systems are highly dependent on the existing fertilizer industry, based exclusively on non-renewable sources – phosphate ores. Such chemical production of phosphate fertilizers represents a very wasteful energy process. In addition, it requires intensive use of natural phosphate and generates waste material that is harmful to the environment. The depletion of phosphate rock reserves leads to the search for new, alternative and environmentally friendly products and processes [1]. One of the proven good and low-cost sources of phosphates for soil remediation is bone meal. On average bone meal contains about 30 % of organic and 70% of inorganic substances. The organic substances are mostly collagen proteins, whereas poorly crystallized, cationic and anionic substituted hydroxyapatite is the main inorganic substance. Animal bone char, the residue after pyrolysis of meat and bone meal, could be an effective phosphorus-rich source that does not contain any potentially harmful sanitary substances [2]. In our research the influence of pyrolysis treatment of meat and bone meal and resulting physico-chemical properties of obtained animal bone char were studied. The pyrolysis of meat and bone meal sample at two different end temperatures (600 °C and 1000 °C) and five different heating rates (5 K min^{-1}, 10 K min^{-1}, 20 K min^{-1}, 50 K min^{-1} and 100 K min^{-1}) was performed. The residues of pyrolysis were characterized by X-ray powder diffraction, IR spectroscopy, elemental CHNS analysis and SEM/EDS analysis. The results of the X-ray powder diffraction analysis showed that the peak intensity of all residues after pyrolysis at end temperature 600 °C, regardless of heating rate, indicate low crystallinity. The weak broad peaks can be attributed to hydroxyapatite. The crystallinity of the samples obtained at pyrolysis of meat and bone meal to 1000 °C was reduced at higher heating rates (50 K min^{-1} and 100 K min^{-1}), with some broad peaks, suggesting that some of the phases present were not well crystallized. The presence of inorganic substances, such as chloroapatite, hydroxyapatite and sodium calcium phosphate, was determined. The most noticeable peak in the IR spectra of residues from pyrolysis at end temperature 1000 °C is at 1027 cm^{-1} and belongs to the P-O bond valence vibrations of the phosphate group in the hydroxyapatite. With residues from pyrolysis at end temperature 600 °C a slight shift to the higher wave numbers (near 1050 cm^{-1}) was observed and points to a different environment in which the P−O bond is located. At 871 cm^{-1} a less intense peak appears, indicating the presence of a carbonate group that was not observed at a higher pyrolysis temperature. The results of the SEM/EDS analysis revealed a strong influence of both pyrolysis end temperature and heating rate on morphology and chemical composition of the final products.

Acknowledgments

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Thermal analysis of synovial fluids in different stages/infections of osteoarthritis

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Keywords: synovial fluid, septic arthritis, differential scanning calorimetry, isoperibolic calorimetry, bacterial strains

The analysis of synovial fluid is an important method in diagnosing and handling septic arthritis. To achieve a quick diagnosis could be a great advantage in the therapy. The DSC (differential scanning calorimetry) proved to be a useful technique in the differential diagnosis of tumours using blood plasma or sera. The aim of this presentation is to show up some characteristic thermal parameters in the diagnosis of different grades of arthritis, which are in good agreement with the severity of disease checked by conventional X-ray supported grading. To follow the effect of different bacterial strains the synovial fluids were inoculated by three different type of bacterial strains (with 10^3–10^5 CFU/mL concentrations) at 37 °C and stored trough 24 hs. After it, they were denatured in 20-90 °C temperature range with 0.3 K/min scanning rate. The change in the maximum denaturation temperature (T_m) and calorimetric enthalpy (ΔH) monitored the severity of sepsis and depended on the type of bacteria. The proliferation characteristics of bacteria should be strain specific. The synovial fluid samples inoculated with the most frequently occurring bacteria were monitored in isotherm mode (isoperibol calorimeter) at 37 °C up to the end of the proliferation. The isoperibolic scans clearly demonstrated specific, concentration dependent representative thermograms in case of each bacterium (duration of proliferation, maximua of proliferation rates etc.). Therefore, thermal analysis of human synovial fluid samples by DSC or isoperibolic calorimetry could be a useful tool in the staging of osteoarthritis and the diagnostics of septic arthritis.

Thermal, structural and morphological characterisation of organic rice starch after physical treatment

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Keywords: Oryza sativa L, thermal analytical techniques, ultrasound

Rice (*Oryza sativa* L.) is a cereal of great economic and nutritional importance due to its expressive consumption. Its contribution in the diet is related to its protein value, but also energetic due to the high content of starch (90% d.b.) [1]. To achieve new properties or improve the characteristics presented by native starch, modifications are carried out, catching the attention of many researchers. Therefore, this study aimed to analyse the effects of ultrasound on the thermal, structural and morphological properties of organic rice starch. The starch was extracted by the aqueous method, followed by alcalase treatment for protein removal [2]. To evaluate the effect of time (15 and 30 min), starch aqueous suspensions concentration (5% and 10%) and amplitude (75% and 100%), the 2^3 factorial design was applied in samples treated by alcalase. The properties of native organic rice starch before and after treatment with alcalase, as well as after the ultrasound treatment were analysed.by thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffractometry (XRD) and field emission gun-scanning electron microscopy (FEG-SEM). The first inflection in the TG curve was related to sample dehydration. Subsequent peaks refer to degradation of the amylose and amylopectin chains, followed by oxidation of the sample. After treatment of the native starch with the alcalase, a reduction in the thermal stability temperature was observed. When physically modified, under greater amplitude of vibration, shorter time and lower concentration, an increase in the thermal stability of the starch was observed. Therefore, the US made possible the increase of the thermal stability of the organic rice starch when greater acoustic cavitation occurred in a more diluted medium, under a short time of exposure. When the starch was treated by alcalase, there was a reduction in the gelatinisation transition temperatures and an increase in the gelatinisation enthalpy (2.5 Jg^{-1} to 3.8 Jg^{-1}). By subjecting these samples to the ultrasound, an increase in T_p was observed and there was no significant difference for enthalpy in most treatments. The concentration influenced the ΔH_{gel} only of the treatments under the lowest amplitude of vibration (75%). XRD revealed the presence and characteristics of the crystalline structure of the starch granules. FEG showed that alcalase treatment was efficient because no proteins were observed in the images. None of the US treatments altered the size and shape of the granules. The use of the physically modified organic rice starch may be an alternative for use as an excipient in the pharmaceutical industry and encapsulating agent in the food industry.

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Thermal analysis in studies of ball milled turmeric and thermooxidation of mustard oil

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Keywords: turmeric nano particles, mustard oil, TG, DSC

Mustard oil obtained from Brassica Nigra (Black Mustard) and Brassica Hirta (Yellow Mustard) has pungent odour and it gives spicy taste to foodstuff. This is a reason behind making it an important ingredient of Indian foods. It is exposed to thermooxidative decomposition while used as a frying medium during food preparation. In the present study, the induction period [1] has been used as a measure to study the oxidative stability of the oil in air and oxygen. It has been found that stability of the oil increases with decreasing partial pressure of oxygen in the reaction atmosphere at lower temperature. In air atmosphere the stability is approximately 3 times higher than in oxygen. At higher temperature, the stability is practically independent of the partial pressure of oxygen. On the other hand, turmeric is the most commonly used Indian spice which is used along with mustard oil during cooking. Turmeric is grinded by the rural folk before adding it to warmed mustard oil. In the present study, mill grinded (5 and 10 hrs) turmeric has been subjected to TGA and then DSC keeping heating rates of 2,4,8 and 16 C min-1. Grinding has been found to bring down the particle size and change its optical properties too. Attempts are made to do the thermooxidative studies after mixing the two.

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Maltodextrin stability: impacts of salt addition, molecular weight and molecular weight distribution on thermal characteristics

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Keywords: maltodextrin; glass transition; temperature; sorption; isotherm; DSC; molecular weight distribution; polydispersity

Powdered mixtures of amorphous and crystalline solids are commonplace in food and pharmaceutical products and ensuring powder stability is a critical and yet, challenging endeavour. In this study, the impacts of salt addition and maltodextrin molecular weight on the physical stability of freeze-dried amorphous maltodextrin-NaCl mixtures were investigated. To build the sorption isotherms, powders were dried or humidified in silica gel or saturated salt desiccators. After equilibration, differential scanning calorimetry was used to analyse the powders' glass transition temperature (T_g) at various moisture contents and the results were fitted into the Gordon-Taylor model. At the same time, the powders' moisture content was determined by thermogravimetric analysis. Powders were then heat treated at 5˚C above T_g to eliminate moisture gradients within the powder before water activity analysis at 25˚C using a dew-point hygrometer [1]. The sorption isotherm results were fitted into the Brunaeur-Emmett-Teller (BET) model. For hybrid maltodextrin-NaCl mixtures, increasing salt content to 10% (wt) did not affect sorption isotherm but significantly depressed T_g. At moisture content of 4% (wb), NaCl addition by 10% (wt) depressed T_g by 12, 14 and 27˚C for maltodextrins of DE 47, 21 and 6, respectively. Comparatively, decreasing the molecular weight of maltodextrin had a greater impact on T_g depression than the 10% (wt) NaCl addition; T_g for maltodextrins of DE 6, 21 and 47 were 151, 86 and 49˚C, respectively.

Next, the thermal characteristics and molecular weight distributions of maltodextrins (DE 6, 21 and 47) were correlated, which aimed to predict the molecular weight distribution in these maltodextrins based on their thermal properties. The molecular weight distribution was characterized using two methods: (1) anion exchange chromatography-refractive index detector to quantify saccharides within the DP-1 to DP-6 range, and (2) size exclusion chromatography-multiangle light scattering detector for saccharides with molecular weight above 1 kDa. Besides thermal properties, molecular weight distribution can also affect a product's mechanical properties and even crystallisation kinetics. Specifically, polymers with higher polydispersity tend to be weaker, more brittle, more elastic and worse at slowing down crystallisation [2, 3]. This could adversely change the texture and stability of food and pharmaceutical products – for instance, a maltodextrin with higher polydispersity can cause lactose and ice to recrystallise in ice-cream quickly during storage, leading to an undesirable gritty texture. The ability to extract polydispersity information from thermograms would aid manufacturers in producing suitable maltodextrins for various applications as well as formulators in troubleshooting and selecting the right maltodextrins for their products.

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Calorimetry

Calorimetric techniques for measuring the fire resistant behaviour of cellulosic textile material functionalized with wastage plant bio-molecules

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Most of the fire retardant chemicals (phosphorous nitrogen based chemicals, halogen based compound) explored for the fire retardant finishing of the cellulosic textile material are not eco-friendly and the treatment process is cumbersome. Hence, there is an increasing demand of the cheap, easily available, eco-friendly fire retardant chemical which after application to the cellulosic fabric, will maintain its physical property like tensile strength, fabric handle, etc. Connected with this theme, wastage plant based bio-molecules named banana pseudostem sap (BPS), coconut shell extract (CSE) and pomegranate rind extract (PRE) have been explored as fire resistant material on the cellulosic polymer. All the treated cotton fabric by BPS showed dramatically less peak heat release rate (PHRR) compared to the control cotton fabric at 35kW/m^2. In addition, maximum average rate of heat emission and the total heat release value of the PRE treated fabric is almost 30% and 60% lower compared to the control cotton fabric. Treated cotton fabric showed 6 (BPS), 8.5 (CSE) and 12 (PRE) times lower vertical burning rate compared to the control cotton fabric. Thermo-gravimetry (TG) curves and the limiting oxygen index (LOI) value revealed that the PRE extract (LOI: 32) treated fabric having more thermal stability compared to the BPP (LOI:26) and the CSE (LOI: 27) treated fabric as it showed higher oxygen index and more weight retention (40%) at higher temperature 450°C.

Thermal studies on mesomorphic binary mixtures

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Binary mixtures of various compounds, capable of forming intermolecular hydrogen bonding are prepared and characterized. The mesogenic 4-nonyloxybenzoic acid is mixed with non-mesogenic compounds viz., aromatic carboxylic acid, aliphatic carboxylic acid and an aromatic pyridine derivative in different weight proportions. All the binary mixtures are found to involve in the intermolecular hydrogen bond formation. All the binary mixtures are found to exhibit induced smectic phases and enhanced nematic phase thermal stability. The thermal span of the liquid crystallinity in binary mixtures are found to enhanced in comparison with the mesogenic 4-nonyloxybenzoic acid. The mesomorphism is observed towards the lower temperatures in binary mixtures. The enthalpy changes across the phase transitions are determined by differential scanning calorimeter at different heating/cooling scan rates. The order of the transitions and the activation energy of transitions are discussed in binary mixtures. The effect of $\pi - \pi$ interactions in stabilization of the mesomorphic phases in the binary mixtures are discussed.

Investigation of the electrocaloric effect by pASC calorimetry

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Keywords: Electrocaloric effect, calorimetry, ferroelectrics.

Electrocaloric materials and caloric materials in general have attracted much attention these last years due to their potential use for future environment-friendly cooling technologies. The electrocaloric effect (ECE) refers to an adiabatic change of the temperature of a polar material when it is subjected to a change in electric field.

Although many indirect approaches have been carried out to determine physical parameters from which the produced heat can be estimated, a direct calorimetric measurement seems to be most adequate for evaluating the electrocaloric performance of a material. During the last decade, a variety of calorimeters have been developed, which allow to measure the adiabatic temperature change or heat flow generated by the sample when applying an electric field. However, many approaches cope with difficulties in achieving perfect adiabatic conditions, so that their reliability is affected [1].

In the presented work, the ECE in polar materials was investigated using a Peltier-element-based adiabatic scanning calorimeter (pASC). This technique has been successfully used for high resolution studies of the heat capacity and enthalpy near phase transition temperature for solids and liquid compounds. The technique requires the use of smaller samples as compared to other calorimeters [2].

As a part of our study, we have verified that pASC can also be used to directly measure the amount of heat absorbed or transferred from the material to the surrounding environment. Measurements have been carried out on ferroelectric samples based on barium titanate. The obtained results on commercial multilayer capacitor showed good agreement with data reported in literature [3].

Direct methods allowing better accuracy measurements of heat and temperature change are highly desired for characterizing electrocaloric materials, particularly for thin film and small size materials. The pASC technique may be a promising approach to achieve this goal.

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Thermodynamic properties of liquid Au-Ga, Ga-In and Au-Ga-In systems determined from calorimetric measurements

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Keywords: Au-Ga-In system, calorimetric measurements, enthalpy of mixing

The Au-Ga-In ternary phase diagram is important for understanding the involved thermodynamic processes during the growth of Au-seeded III–V heterostructure nanowires containing In and Ga (e.g. Au-seeded InAs/GaAs nanowires) [1, 2]. Using calorimetric method the Au-Ga, Ga-In and Au-Ga-In systems were investigated. The drop calorimetric measurements for all metallic systems were carried out at three temperatures: 1223, 1323 and 1423 K. The ternary liquid Au-Ga-In system was investigated along the following cross-sections: X(Au)/X(Ga)=1:1 and X(Ga)/X(In)=1:1. Integral enthalpies of mixing of liquid alloys were determined. Obtained experimental data were used to find ternary interaction parameters by applying Redlich-Kister-Muggianu formula for the description of liquid solution. The obtained results are compared with the results of calculations of Au-Ga-In system done by Ghasemi et al [3]. However, since thermodynamic data for ternary Au-Ga-In system do not exist, these calculation were performed using respective binary data and ternary data for solid phase.

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Combustion behaviour and thermal stability of TPU composites using layered yttrium hydroxide and graphene oxide as flame retardant materials

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Keywords: Layered yttrium hydroxide, Flame retardant, TPU, Nanocomposite, Graphene Oxide

A kind of layered yttrium hydroxide(LYH) and its graphene oxide composites were synthesized through a co-precipitation method. X-ray diffraction(XRD), Fourier transform infrared spectra(FTIR) and transmission electron microscope(TEM) were used to evaluate the structures of the composites, the results demonstrated that LYH was homogeneously dispersed on GO sheets. TPU/LYH and TPU/GO-LYH composites were then prepared by melt-blending method. The morphologies and structures of the composites, revealed by Transmission electron microscope (TEM) and Scanning electron microscope(SEM), ascertained that GO-LDHs can be better dispersed in TPU owing to strong interaction from the hydrogen bonds between oxygen-containing groups and hydroxyl. The fire retardancy of TPU composites were evaluated using cone calorimeter test(CCT), Thermo Gravimetric Analyzer text(TGA), which illustrated that the heat release rate and smoke produce rate of TPU system declined significantly. The improved flame retardancy and smoke suppression maybe attributed to the physical barrier of graphene oxide and the catalytic carbonization of the composites by char analysis.

Acknowledgments

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Fast and low-cost calorimetry method based on infrared thermography for Phase diagrams estimation

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Keywords: Phase diagrams estimations, Differential Scanning Calorimetry, Infrared Thermography, Thermodynamic modeling

Phase diagrams are a primordial tool in materials science. They are used for materials synthesis, the understanding of their behavior and their macroscopic properties. To establish the phase diagrams of materials, the most common methods used are Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) but the determination of a reliable phase diagram via those standard methods is very time consuming and poorly adapted to screening procedures. An innovative phase diagram estimation method (IRT-method) was first developed in the framework of the European FP7 Research Project SAM.SSA (2012-2015) for the fast screening of simple binary systems (polyols binary systems in which only melting and eutectic transitions occur) [1].

In the framework of the European Interreg Sudoe SUDOKET (2018-2021), we are currently improving and adapting IRT-method to binary systems presenting more complex phase diagrams including peritectic, metatectic transitions (fatty acids and/or fatty alcohols binary systems). IRT-method allows establishing their preliminary phase diagrams in only a few hours instead of several weeks.

Even if this method was developed and is being adapted and improved in the frame of thermal energy storage applications, it could be extended to any application which requires the development of new materials as well as screening steps. To extend this innovative calorimetry method to other applications, it must be affordable (less than 10k€ for a whole setup). Consequently, the objective is to equip the experimental setup with a low-cost infrared camera (for instance, Optris PI 450, Detector: FPA, Resolution: 382x288, Spectral range: 7.5-13µm) instead of the expensive high-end camera (FLIR X6580sc, Detector: cooled InSb, Resolution: 640x512, Spectral range: 1.5-5µm) used until now while keeping high-quality results.

The experimental setup fundamentals, the experiments, the numerical data treatment and the complexity of the obtainable phase diagrams are presented and assessed in this work. The phase diagrams of the 1-Hexadecanol/1-Octadecanol, 1-Hexadecanol/Myristic acid and Palmitic acid/Stearic acid binary systems estimated with both low-cost and expensive methods are shown. Both methods are validated by comparing obtained results with data extracted from literature [2-3], with experimental data obtained using DSC and with thermodynamic modeling results [4]. Finally the reachable performances and the limits of the low-cost calorimetry method compared with the expensive one and DSC are discussed.

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Thermochemical behavior of some 3d Transition Metal-Antimony compounds by high temperature direct synthesis calorimetry

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Thermoelectric materials have the potential to save energy by recycling the waste heat from many processes. These materials are under active alloy development and consequently an understanding of the thermodynamics and phase equilibria of these systems is necessary. In this work we have performed a calorimetric investigation of some thermoelectric alloys, which are useful for energy savings, but do not contain toxic or extremely rare elements. The standard enthalpies of formation of some binary antimony and transition metal (TM)

Compounds have been measured by high temperature direct synthesis calorimetry. The reported results are: ScSb(–112.0 ± 3.1); TiSb (–63.3 ± 2.4); CrSb (–3.0 ± 2.7);
Mn_2Sb –9.2 ± 1.5); CoSb (–19.6 ± 1.3); $CoSb_3$(–20.1 ± 2.0);NiSb –28.9 ± 1.8). In kJ/mole of atoms.

We will compare our results with some previously published measurements. We will also compare the experimental measurements with predicted values by the ab initio calculations.

Calorimetric measurements in the liquid Cu-In-Sn-Zn quaternary alloys relevant for Pb-free solders

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Keywords: Pb-free solders; enthalpy of mixing; free enthalpy of mixing; Geometric models; Cu-In-Sn-Zn quaternary.

The results of the measurements and calculations of thermochemical properties such us enthalpies and free enthalpies of mixing in liquid state for Cu-In-Sn-Zn quaternary alloys at high-temperature using Tian-Calvet calorimeter and the general solution model of Chou are presented in this work. The traditional geometric models such as Kohler, and Toop are also included in calculations for comparison and discussion.

The values obtained by a symmetric model (Kohler) are more exothermic than those obtained by Toop's model and the experimental ones. The results obtained by Chou's model show that Cu-In-Sn-Zn quaternary system is asymmetric.

On the other hand, the results obtained for Cu-In-Sn-Zn quaternary alloys are also compared with those obtained previously for the two Ag-In-Sn-Zn and Au-In-Sn-Zn quaternary systems. Cu-In-Sn-Zn presents an exothermic enthalpies and free enthalpies of mixing.

Thermo-kinetic studies on azodicarbonamide/potassium periodate airbag gas generants

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Keywords: Airbags, Azodicarbonamide, Potassium periodate, DSC-TGA, Tank Testing

The azide based fuel/oxidizer mixture generally used in the airbag gas generants are reported to have serious health issues on the occupants being highly toxic [1]. This work attempts a potential alternative Non-azide,Non-toxic fuel/oxidizer mixture consisting of azodicarbonamide ($C_2H_4O_2N_4$) and potassium periodate(KIO_4) which can replace the conventional toxic NaN_3/KNO_3 airbag gas generants with the same performance characteristics. Initially different weight compositions of $C_2H_4O_2N_4/KIO_4$ were subjected thermal analysis using DSC-TGA to arrive at an optimal weight composition. The thermochemical properties such as onset temperature to exothermicity, peak temperature of decomposition, heat energy liberated and the residual mass analysis of optimal mixture of $C_2H_4O_2N_4/KIO_4$ gas generants were measured using DSC/TGA. Then these parameters were compared with thermochemical properties of existing conventional NaN_3/KNO_3 airbag gas generants [2]. It was found that the residual masses remaining after decomposition were found to be almost zero compared to the NaN_3/KNO_3 airbag gas generants. The Thermo-kinetic parameters such as activation energy and Arrhenius factor were also estimated for the DSC data using Ozawa and Kissinger methods. The tank testing of the optimal composition is performed to obtain the ballistic properties such as peak pressure on detonation and time to peak pressure on detonation, which are major performance parameters to be evaluated during the performance testing of an airbag gas generant.

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Elucidating the Metabolic machinery of S. Zooepidemicus For hyaluronic Acid production using calorespirometry

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Keywords: Heat compensation calorimeter, Respirogram, S. zooepidemicus

Hyaluronic acid (HA) is a linear chain value-added biopolymer finds extensive application in cosmetic, biomedical and nutraceutical industries. Fermentative production of HA by *Streptococcus zooepidemicus* was successfully monitored using Heat compensation calorimeter by supplementing different initial glucose (10–60 g/L) concentrations, their implications on metabolic machinery and thermodynamics of biochemical conversion were dealt in this study. The heat flow signal resulting out of overall cellular metabolism of *S. zooepidemicus* corroborated well with the respirogram (Carbon di-oxide Evolution Rate). The thermogram fingerprinted various stages of cell growth and similar comparison plot of respirogram would serve as an additional analytical tool for an estimation of unknown stoichiometric coefficients of the overall biochemical conversion. Modelling of heat rate signal was accomplished by fitting with a modified logistic equation, which reliably predicted the growth rate and duration of logarithmic phase from the real-time measurements. Variation in specific growth rate (μ) was observed between 0.29 –0.411 $h^{–1}$ although the fraction of carbon channelled to various metabolic pathways remained highly conserved irrespective of initial carbon load i.e. yields of biomass, HA and lactic acid remained fairly constant in all runs. Thermodynamic study revealed that the growth of *S.zooepidemicus* was significantly driven by enthalpic change and remained to be the first study of this kind. Gel Permeation chromatography elucidated that the obtained HA was in high molecular weight range of1.45–1.6 MDa.

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The Influence of Laser Biotechnology on calorific (Energetic) Value of THE PLANT Biomass

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Keywords: laser biotechnology, biomass, rose multiflora, calorific value, energy

One of the most promising alternatives to meet the increasing demands of the human population for energy sources is the production of bio-energy from biomass of plants. Wide scale studies strongly support the development of the different sources of bioenergy and biofuel production. Application of environmentally friendly laser biotechnology could be applied for more efficient increase of biomass for bio-energy production by using sustainable thermo, thermo-chemical, plasma and bio technologies. The increase of the biomass production on energy plantations as a result of laser photostimulation/irradiation of plants cultivated in suboptimal environmental conditions (e.g. on contaminated soil as well as application of similar method for increase of biomass production in hydro-botanic wastewater treatment plants) could contribute to promotion of low carbon energy production and sustainable development in different regions and countries. Several studies were undertaken to evaluate the effect of laser photostimulation/irradiation not only on growth rate of plant biomass but also on calorific (energetic) value. One of the remarkable example was a study of energy recovery from three groups (control, laser stimulated (3times/3sec) and laser stimulated 3times/9sec) of *Rose multiflora* biomass after 5 years field experiments. A laser stimulation/irradiation was conducted using the Medical Laser (D 68-1) emitted red light with a wavelength of 672 nm and λ power of 20 mW on *Rosa multiflora*'s cuttings by the application of two exposure times intermittent: a) 3times x 3 seconds, and b) 3times x 9 seconds. Exposed seedlings along with control group (non-irradiated) were planted in spring of 2009, the spacing of 70 x 70 cm. in leached brown soil. In this study, a calorific value was determined by using a bomb calorimeter (Model: KL-12 Mn), following European Standard PN-EN 14918:2010 and PN-ISO 1928. The energy content of *Rose multiflora* biomass control (without laser stimulation) group was 17.574 MJ/kg while laser stimulated 3times/3sec and 3times/9sec groups were 18.255 and 17.698 MJ/kg. From the results above, it can be noted that in comparison with control group and laser stimulated for 3times/9sec, the highest calorific value of the pant biomass was achieved using laser stimulation for 3times/3sec (18.255 Mj/kg). Hence, it is worth to emphasize that proper selection of the algorithms of laser biotechnology could increase a calorific value of plant biomass which is an essential factor for qualitative conversion of plant biomass into value-added bio-energy. There are also real perspectives for wide-scale application of laser biotechnology for more intensive biomass production under suboptimal conditions.

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Differential scanning calorimetry as a thermoanalytical technique in observing the evolution dispersed droplets of concentrated W/O emulsion

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Keywords: DSC, concentrated emulsion, dispersed droplets, freezing temperature, droplet size distribution

In this work the evolution of droplets formation in highly concentrated emulsion system was observed using Differential Scanning calorimetry, DSC. Water-in-oil, W/O emulsions were prepared by dispersing drop by drop of 75% (v/v) internal aqueous phase into the rapeseed oil continuous phase at room temperature using rotor stator homogenizer. The droplets formed during: (1) emulsification; (2) shelf-life (3) and breaking process were observed by determining the mean freezing temperatures, T*. The samples were gently cooled-down below its solid-liquid equilibrium temperature, T^{SL} then heated back to above its melting temperature, T_m. Energy released during freezing was recorded in order to get information about the water droplet dispersion state. Mean droplet size distribution in volume, D_{43} was correlated to the freezing temperature T* and the morphology was monitored using optical microscopy. The results indicated that DSC so far has been very promising technique to follow the evolution dispersed droplets of concentrated W/O emulsions.

Cements, building materials

The effect of milled fluidized catalytic cracking catalyst waste on calcium aluminate cement hydration and structure formation of binder

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Keywords: calcium aluminate cement, FCCC waste, hydration, XRD, calorimetry, microstructure

In this work, the hydration of calcium aluminate cement (CAC, Al_2O_3>70%) binder mixtures with additives (0%, 1%, 5% and 10%) of non-milled fluidized catalytic cracking catalyst (FCCC) waste and milled FCCC waste was investigated. The methods of calorimetry, thermal analysis, XRD, SEM, as well as compressive strength evaluation were used. SEM and XRD analysis tests were also carried out for binder after it thermal treatment at the temperatures of 110°C and 1200°C. Milled and non-milled FCCC waste was found to shorten the induction period of the CAC hydration and accelerates the time of the secondary heat release effect, especially in specimens with the highest content of FCCC waste. However, the results obtained show differences in the effect of milled and non-milled waste on the formation of the structure of binder during its hardening and after firing in high temperature. SEM tests revealed significant changes in CAC binder microstructure caused by the added 5% and 10% of the milled FCCC.

Analysis of the properties of foamed geopolymers modified by the addition of expanded perlite

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Keywords: thermal conductivity, thermal insulation materials, civil engineering, absorbability, compressive strength

Reducing energy consumption is one of the ways to decrease environmental pollution resulting from energy production. The use of thermal insulation materials in commercial and industrial buildings reduces the energy expenditure on heating and air conditioning of buildings. Geopolymers are one of example of newly developed materials which can be widely used for various construction applications also as thermal insulation.

This paper presents the results of analyses of the influence of the volume share of expanded perlite introduced in an amount of 30 vol.% or 50 vol.% to the foamed geopolymer based on metakaolin on the thermal insulation properties of such a composites. A foamed geopolymer without additives was used as a reference material. Moreover, for all samples density, absorbability and compressive strength were examined. The obtained results confirmed the beneficial effect of the introduction of perlite expanded into the geopolymer matrix on increase the thermal insulation properties.

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Resistance to carbonation of zeoslag by accelerated test using thermal analysis

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Keywords: concrete, k-value, mortar, carbonation, accelerated test, thermal analysis

The research was oriented a) to prove the suitability of ZeoSlag as a Type II addition for use in concrete with the intention of alternating scarce granular blast-furnace slag, both for the evaluation of pozzolanic reactivity and confrontation of the determined ZeoSlag properties with the criteria in STN EN 15167-1 [1]; b) to determine the ZeoSlag k-value in 5% to 40% mass CEM I 42,5 R substitute according to the TSÚS methodology based on TNI CEN/TR 16639 [2] in compliance with standard requirements for concrete, as given in STN EN 206 + A1 [3]; c) to k-value verification by the tests specifying c1) basic Aspects of durability (28- and 90 days compressive strength, water absorption and resistance to water penetration under pressure) and c2) specific Aspect of durability – carbonation resistance based on an accelerated carbonation test (ACT) according to the TSÚS methodology. The ACT was performed for 28 days in (20 ± 1) °C/20 % vol. CO2/50% R. H. – air exposure. The complex assessment consisted of registered changes in weight, length, bulk density, dynamic modulus of elasticity and strengths over time, determined pH values of water extracts and evaluated chemical, X-ray diffraction and thermal (TG-DTA) analyses. TG-DTA analysis provided a degree of carbonation, which was evaluated from the ratio of the carbonated CaO to the total CaO present in the specimens after the ACT as compared to that after the reference (20 ± 1) °C/50 % R. H. – air cure. On the basis of the obtained results, the accuracy of the k-value determination in relation to the degree of impact of the XC environment according to STN EN 206 + A1 was checked by the change criteria Δc in the measured properties. The way of our evaluation quantifies weight changes, shrinkage, dynamic modulus of elasticity, compressive and flexural strength as well as the degree of carbonation after the ACT calculated from TG-DTA tests and chemical analysis. Our evaluation method provides for the change criterion Δc based on the relevant standards for the design of concrete STN EN 206 + A1 and STN EN 1992-1-1 Eurocode 2 [4] and tightens the given criterion of CEN/TR 16639 related to a carbonation resistance. Herein the use of national prescriptions and regulations for determining main utility properties (strength uptakes, water absorption and resistance to water penetration under pressure) and durability aspects (resistance to carbonation, chloride penetration, sulphate attack, freezing and thawing and to the action of de-icing salts) is susceptible [2]. This paper introduces all obtained results and analyses the potential utilization of ZeoSlag as Type II addition with the determined k-value for use in concrete and points to its carbonation resistance based on the ACT results with special emphasis on the use of TG-DTA technique for this purpose.

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Phase composition of ceramic based alkali-activated polymers – combination of X-ray diffraction and thermal analysis

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Keywords: alkali activation, geopolymer, waste ceramic, zeolite

Alkali-activated aluminosilicate materials (geopolymers) are widely studied as potential binder for concrete, fire resistant material, coating or as medium for solidification of hazardous wastes [1]. Wide range of aluminosilicates can be used as precursor for alkaline activation; they can be of natural origin (e.g. volcanic scoria), industrial wastes or by-products (coal fly ash, biomass ash, blast furnace slag, mine tailings) or intentionally produced materials (metakaolin). The present paper deals with alkaline activation of waste red-clay ceramic; the studied ceramic precursor comes as waste from brick production, but "brick and tiles fraction" of Construction and Demolition Waste can be activated as well [2].

Very complex mineralogical composition is typical for red-clay ceramic; it contains numerous silicates (feldspars, clay minerals), quartz, hematite and considerable portion of amorphous phase. The latter one is supposed to be activated by an alkaline solution to provide a geopolymer product. Within this study, the ceramic precursor was activated by solution of sodium silicate; a used range of silicate modulus of activator (SiO2/Na2O molar ratio) was 0.8 to 1.5; samples were cured in laboratory condition as well as in 60 °C. The obtained products were characterized by means of compressive strength, pore size distribution, thermogravimetry and phase analysis. Geopolymers are fundamentally amorphous and thus obviously "invisible" for X-ray diffraction. Nevertheless, the XRD is able to quantify present mineral phases as well as the amount of amorphous matter. A new method for estimation of composition of amorphous product of alkaline activation was proposed. The amount of chemically bound water in geopolymer was measured by help of TG-EGA (Evolved Gas Analysis), the content of other oxide constituents (SiO2, Na2O, Al2O3, CaO) was calculated on base of elementary balance between input raw materials and activated product, which "crystalline" components were characterized and quantified by XRD.

The thermal treatment is well known to increase strength of geopolymer cement [3]. The performed phase analysis revealed that crystallization of zeolite minerals from the initially amorphous activated matter take place during the thermal treatment, being responsible for the strength increase. Sodalite and chabazite were identified in dependence of activator composition.

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Effects of the heat annealing in the properties of fibrous aerogel insulation

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Nowadays, the application of thermal insulation materials both by existing and by new buildings is one of the most important actions in order to reduce the energy loss of buildings. Besides the use of the conventional insulations (plastic foams and wool materials) aerogel is one of the most promising thermal insulation material. Aerogels, one of the lightest solid materials available today, are manufactured through the combination of a polymer with a solvent forming a gel. For buildings the fibre-reinforced ones are the mainly used types. It is produced by adding the liquid-solid solution to the fibrous batting. In this paper, changes in the thermal performance, as well as, in the material structure of the aerogel blanket will be followed after thermal annealing. The samples will be put under isothermal heat treatments at 70 °C for weeks and also they will be put under thermal treatment at higher temperatures (till 250 °C) for 1 day. Once the changes in the sorption properties resulted by the heat annealing will be presented. Furthermore, the changes in the thermal conductivity will be followed by Holometrix Lambda heat flow meter. While the changes in the structure and in the surface of the material due to the heat treatment will be investigated by X-ray diffraction as well as with Scanning Electron Microscopy. Besides that above mentioned measurements, results of Differential Scanning Calorimetry will be presented, as well.

Thermal analysis of ceramic-based geopolymers exposed to accelerated carbonation

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Keywords: geopolymers, ceramic waste, thermal analysis, accelerated carbonation

Geopolymers are environmentally friendly binders usually prepared by activating industrial waste products or naturally occurring alumino-silicates with an alkaline hydroxide and/or silicate solution. As their production is very different compared to Portland cement, this new generation of binders has a high potential not only to lower the prices of binders, but mainly to decrease the significant carbon footprint which originates during the production of traditionally used ordinary Portland cement. Similarly to concrete, several pozzolana active materials, such as fly ash, blast-furnace slag, silica fume or metakaolin were successfully incorporated into geopolymers. Nevertheless, the utilization of fine ceramic waste powder, also pozzolana active, in geopolymer production has rarely been reported. In this paper, several ceramic-based geopolymers are prepared with the utilization of ceramic waste powder, alkali activated by the mixtures of sodium hydroxide and sodium silicate with the silicate modulus ranging from 0.8 to 1.4. The studied samples are thermally cured within the first 7 days at temperatures of 20 °C and 60 °C, respectively, and thereafter, they are exposed to 20±2% CO_2 at 85% RH for the period of 10 months. The effect of the accelerated carbonation conditions on the composition changes and thermal stability of the studied materials was determined by means of X-ray diffraction and thermal analysis (DSC/TG). These results are supported by evolved gas analysis. Mechanical properties, such as compressive and flexural strength are determined. The accelerated carbonation conditions along with higher curing temperatures led to an enhancement of mechanical properties and non-negligible composition changes of all studied ceramic-based geopolymers compared to those stored in laboratory conditions.

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Changes in structure and composition of gypsum paste at high temperatures

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Keywords: gypsum, high temperatures, microstructure, SEM, XRD, EGA

The behaviour and structure of the gypsum at high temperatures was investigated by the means of SEM, XRD, TG and EGA. The gypsum paste samples were heated to temperatures from 50 °C to 1000 °C. It was found that the changes in the structure of gypsum are in good accordance with the changes of mechanical properties. The crystals of calcium sulphate dihydrate are disrupted at the temperature between 50 to 100 °C and the strength decreases significantly, after heating to 700 °C the crystals starts to be larger and packed closer to each other and the strength increases again. After heating to 1000°C the strength is nearly the same as the strength of unheated material. The decomposition of gypsum starts at 1000 °C, according EGA analysis.   The results of XRD shows, that the changes of calcium sulphate forms (dihydrate to hemihydrate and then to different modifications of anhydrite) are not sudden but occurs gradually and different forms of calcium sulphate exists in the heated gypsum paste together. The results of TG and XRD are also strongly depending on the heating conditions and the age of the sample, because some modifications of anhydrite are unstable and could rehydrate to hemihydrate after some period.

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Ceramics, glasses

Crystal growth in chalcogenide glasses – combination of direct and indirect experimental methods

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Keywords: crystal growth, thermal analysis, microscopy

Crystallization process plays a key role in preparation, processing and application of amorphous materials. The crystallization process needs to be prevented to obtain an ideal amorphous material, or, on the other hand controlled transformation from the amorphous to the crystalline state is a cardinal process of the considered technology. The crystallization process consists of two stages – nucleation and growth. Understanding of these processes is then a fundamental phenomenon, either to prevent or control the amorphous-to-crystalline transformation. Several direct and indirect methods for studying crystallization can be found in the literature. The most applied techniques of thermal analysis (TA) to study crystallization process are differential thermal analysis (DTA) and differential scanning calorimetry (DSC) [1]. These methods are powerful and certainly provide valuable kinetic results in case that the heat evolution associated with crystallization can be measured reliably. Another TA technique is thermomechanical analysis (TMA) [2], which can be advantageous in cases when the heat evolution during crystallization is below detection limits of conventional DSC or DTA. Another experimental approach to study crystallization is based on direct observation of formed crystals using microscopic techniques (optical and electron microscopy) [3].

An extensive study of crystal growth in chosen Ge-Sb-Se chalcogenide glass will be shown in the contribution. Direct measurements of crystal growth rates using microscopy are combined with viscosity obtained by TMA and thermal properties measured by DSC to predict the crystal growth behavior in wide temperature range. In addition the crystal growth rates are calculated from isothermal DSC experiments and compared with the data obtained from the direct measurements using microscopy. This combination brings a relatively easy technique to obtain the crystal growth rates form the DSC measurements.

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Optical characterization of nanostructured se-te-bi thin films

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Keywords: Glasses, nanostructured, nanorods, thin films, band gap

This paper reports the synthesis and optical characterization of thin films of $Se_{80-x}Te_{20}Bi_x$ ($0 \leq x \leq 12$) glassy alloys containing nanorods. The amorphous samples were prepared using melt quenching method and thin films of these samples were fabricated using thermal evaporation technique. The structural characterization of thin films was carried out using XRD, SEM and TEM. The XRD studies revealed that samples are amorphous in nature while SEM and TEM results indicated the formation of nanorods of diameter 30-100 nm. The absorption and transmission spectra of these nanostructured films were recorded on UV-Vis spectrophotometer. Various optical constants including energy band gap, refractive index, extinction coefficient etc. were calculated. The results show that energy band gap decreases while refractive index and extinction coefficient increases on increase in Bi concentration in Se-Te-Bi nanostructured system. Further, it was observed that nanostructure formation leads to decrease in band gap values as compared to bulk Se-Te-Bi thin films.

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Application of thermal analyses (TG-DTA, DIL, TMA) to study of Glazes

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Keywords: glaze-ceramic body system, thermal analyses, set point, glass transition temperature, SciGlass

Ceramic materials as well as any other types of materials are prone to thermal stresses, the first equations and treatments of thermal stress deterioration of ceramics were published hundred years ago [1]. The study of a glaze – ceramic body system is currently attractive due to new testing methods developed, especially with regard to the development of glazed ceramic systems and the even increasing quality requirements of the final product. Several methods and devices have been developed during the comprehensive study of the ceramic body – glaze system for the determination of stress relations and the evaluation of the coefficients of thermal expansion [2-4].

Characterization of the properties of the glaze and the body during thermal loading and the possibility to compare the results of the individual methods of thermal analysis is crucial for the evaluation of the state of stress relations of ceramic body – glaze system and identification of causes of damage of building ceramics or historical ceramic products. Glazed ceramics or porcelain must be designed to withstand the conditions of the environment without defects. Furthermore, using of thermal analyses and their combinations could be useful for the consideration if the glaze was inappropriately chosen for the given type of body or if the disorder of a glaze is due to improper usage or storage. The evaluation of stress relations and the identification of defects could detect past production faults. The use of thermal analyses methods can also contribute to study and the development of new glazes, where the evaluation of software-designed easily prepared compositions (from several types of operating glazes and colorant suspensions) of glazes is lengthy. This work mainly is focused on the comparison the suitability of individual types of thermal analysis methods and the possibility of measuring different types of samples (compact, fine powders, samples taken from damaged ceramic products etc.) The authors have undertaken attempts to evaluate all the characteristic thermal properties (CTE, transition temperature, set point of the glaze) and to determine the stress relations of already used ceramic products and newly designed glazed ceramics. Moreover the opportunity of using software-calculated thermal properties has been verified.

Data obtained by dilatometric measurement were compared with software calculations of CTEs and data measured by thermomechanical analysis. The curves of the representative model systems show that the relative expansion data of glazes measured by both analyses at the same measuring conditions are very similar and so can be both used for the evaluation of the glaze – ceramic body fit. The values indicate good agreement between these two experimental methods. The range of values of CTEs is relatively small and confirms the suitability of using calculated CTEs for the evaluation of stress relations. Value deviation for individual measurements and calculations did not exceed 10 rel%.

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Thermodynamics of glass formation in Pt-based bulk metallic glasses

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Keywords: critical cooling rate, Gibbs free energy difference, multi-component alloys, TTT diagram, glass forming ability

In recent years, many bulkmetallic glass (BMG) forming multi-component alloys have been synthesized. Among them, Pd-based BMG's like ternary Pd40Ni40P20and quaternary Pd43Cu27Ni10P20systems have been found to be among best glass formers with remarkably low critical cooling rate, Rc. The value of Rcfor Pd40Ni40P20is found to be 1.57K/s [1] with critical thickness of 7 mm [2], but the addition of Cu as fourth element forming Pd43Cu27Ni10P20decreases the Rcvalue required for glass formation to 5 x 10-3K/s [3] resulting in a critical casting thickness of > 72 mm [1]. Addition of fourth element enhances the glass forming ability (GFA) corroborating the so-called *confusion principle*put forward by Lindsay Greer [4].

Looking at the similarities between Ptand Pd, new series of Pt-based ternary and quaternary systems viz., Pt60Ni15P25and Pt57.3Cu14.6Ni5.3P22.8bulk metallic glasses have been recently reported [5-6]. In this talk, critical cooling rate Rc derived forPt60Ni15P25 using the nose of TTT diagram will be discussed. In constructing TTT diagram, a simple hyperbolic variation [7] of ΔCpinserted into the expression of Gibbs free energy difference, ΔG has been used. The so-obtained Rcis 9.39 x 10-5K/s almost exactly matches with the experimental value of 9.2 x 10-5K/s.

The driving force of crystallization, ΔG has also been evaluated for Pt57.3Cu14.6Ni5.3P22.8BMG and assumption of a different hyperbolic variation of ΔCp [8] provides values quite close to experimental ones in the entire range of under-cooling.

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Study of thermal behaviour and photoluminiscence properties of Er and Nd doped yttrium aluminate glasses

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Keywords: thermal behaviour, photoluminescence properties, aluminate glasses

Yttrium aluminate glasses with high alumina content doped with a transition metal or lantanide elements, such as Er or Nd, are important and promising solid-state laser materials with possible applications in luminescence systems, window materials for a variety of lamps and ultimately for fiber-optic telecommunication systems. However the specific luminescent properties of laser materials are highly sensitive to changes in dopant concentration, host stoichiometry and processing conditions. Moreover, the laser applications require homogenous and highly transparent materials. In this work yttrium aluminate glasses (76.8 mol.% of Al_2O_3, 23.2 mol. % of Y_2O_3) doped with Er^{3+} and Nd^{3+} ions at different concentration level (0.25 mol.%, 0.5 mol.% and 0.75 mol.%) were prepared by flame synthesis in form of glass microspheres. The prepared samples were characterized by SEM and XRD analysis. For study of thermal behavior of prepared systems, DSC analysis in temperature interval 35-1200°C, with heating rate 10°C/min were performed in nitrogen atmosphere. The list of prepared samples and basic properties are shown in (**Table 1**). The two exothermic effects (≈940, ≈1010°C) which can be assigned to crystallization of YAG phase in two steps were observed in DSC records of all prepared samples. The high temperature XRD measurements were performed in temperature interval 600-1200°C, with heating rate 5°C/min for more detailed study of thermal behavior of prepared systems and for study of temperature dependence of YAG content in samples during thermal treatment. In whole temperature interval only YAG phase crystallization was observed. Based on excitation spectra of Er- and Nd-doped samples measured in the interval 250-750 nm, appropriate excitation wavelengths (380 nm for Er- and 360 nm for Nd- doped samples) were selected. The emission spectra were measured in VIS and NIR region in case of Er doped samples and in NIR region in case of Nd doped samples. All measured emission spectra (PL) consist of characteristic bands due to the typical 4f-4f transitions within Er and Nd ions. From comparison of measured intensities is evident, that the highest intensities were obtained for 0.5 mol. % Er doped sample (in both, NIR and VIS spectral regions). In the case of Nd doped samples, the maximum intensity value was found for the sample at doping level of 0.75 mol.% of Nd. Also, the crystallization experiments were performed at 1000°C and 1500°C with sintering time 20, 40 and 60 min. PL spectra of crystallized samples were measured and the dependence of PL intensities on YAG content was studied.

Table 1: The list of the samples and their basic characteristics

sample	Al_2O_3 [mol.%]	Y_2O_3 [mol.%]	Er_2O_3 [mol.%]	Nd_2O_3 [mol.%]	T_{p1} [°C]	T_{p2} [°C]	XRD
A6Y4Nd0.25	76.8	22.95	0.00	0.25	941	1010	amorphous
A6Y4Nd0.50	76.8	22.70	0.00	0.50	941	1011	amorphous
A6Y4Nd0.75	76.8	22.45	0.00	0.75	940	1012	amorphous
A6Y4Er0.25	76.8	22.95	0.25	0.00	941	1008	amorphous
A6Y4Er0.50	76.8	22.70	0.50	0.00	941	1008	amorphous
A6Y4Er0.75	76.8	22.45	0.75	0.00	941	1012	amorphous

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The effect of LiF on the thermal stability and thermoluminescence properties of borosilicate glasses

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Keywords: Oxyfluoride glass, LiF, borosilicate glass, thermoluminescence TL, high-energy radiation

Lithium fluoride has structure analogous to NaCl but it is much less soluble in water. Because of the wide and direct band gap for LiF (13.6 eV), its crystals are transparent to short wavelength ultraviolet radiation, far more than any other material [1]. Therefore, lithium fluoride crystals can be used as a means to record ionizing radiation exposure for gamma rays, beta particles and neutrons in thermoluminescent dosimeters (TLDs) [2-4]. However, LiF is toxic and it is impossible to use this material in biological environments. In some cases, i.e. brachytherapy, special detectors measuring ionizing radiation inside biologic tissues is required [5]. The first crucial feature of ionizing radiation detector is similar to human tissue equivalent absorption coefficient. It is necessary to use a detector which has similar effective atomic number (Z_{eff}) [6]. It turns out that modified borosilicate glasses can be characterized by similar shielding parameters as for human organs [7-8]. Moreover, the elemental composition of batch has the principal influence on final thermoluminescence properties [9]. Due to the well known luminescence properties of crystalline LiF we developed a new LiF-B_2O_3-SiO_2 glass and glass-ceramics based on this system. The effect of LiF admixture on thermal stability of the glass is studied. We analysed thermoluminescence properties of the oxyfluoride glasses in conjunction with their thermal stability and tendency to crystallization of LiF-phases. Glow curves shape are presented and compered to currently used dosimetric materials. Results showed that the increase of lithium fluoride content in the borosilicate glass causes the efficiency enhancement of thermoluminescence signal. Moreover, controlled crystallization of the oxyfluoride glasses can further enhance the intensity of thermoluminescence phenomena.

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Peculiarities of foam glass synthesis from natural silica-containing raw materials

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Keywords: foam glass, pipeline protection, Russian Far East, diatomite, foaming

The safety of pipelines highly depends on the quality of corrosion protection. The soil has an aggressive impact on the pipe wall from the outside. External protection is designed not only to preserve the integrity of pipes, the quality of petroleum products and the speed of their transportation but also to protect people's health and the environment. Therefore, there are additional requirements on external protection: prevention of formation of condensate and high temperatures on the pipe surface; prevention of temperature losses leading to oil freezing in the pipe; minimal environmental impact. Taking into account all the listed requirements, the only suitable choice now is foam glass – a heat-insulating material, which is highly porous glass. Along with excellent thermal insulation properties and complete environmental, fire and hygienic safety, foam glass has the following list of advantages: durability, incombustibility, ease of handling and installation, stability, resistance to atmospheric and biological effects, etc. In addition, foam glass materials can be obtained on the basis of a wide range of raw materials. Any large-scale production requires a local raw material base. The possibility of using amorphous silica-containing raw materials in foam glass technology is confirmed by a number of studies [1-3]. As part of the studies [4-5], it was found that the foaming of mixtures with a high content of natural silica-containing raw materials differs from the foaming of glass waste. So, it is necessary to study the porous structure formation mechanism and the influence of the main raw material and the foaming agent composition on this process. In this regard, this article discusses the peculiarities of diatomite raw materials foaming using a new foaming agent– sodium hydroxide – which is atypical for foam glass technology. The article describes the silicate materials foaming mechanisms using various types of foaming agents: carbon, carbonate, hydrate. The factors justifying the choice of a specific type of a foaming agent are given. It is shown that when using natural silica-containing raw materials, hydrate foaming is promising. The process of preparing raw materials, the heat treatment mode and the properties of the obtained materials are described. The dependence of the material structure and properties on the composition of the batch, synthesis parameters and the presence of modifying additives is analyzed. Using the DTA method, physical-chemical processes occurring during the batch foaming (removal of physically and chemically bound water, recrystallization, melting) are considered. Using the XRD method, the phase composition of the samples is represented by an X-ray amorphous glass phase and α-quartz crystals. It is concluded that the use of a new type of foaming agents is promising in the preparation of porous silicate materials using foam glass technology.

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Cultural heritage

Characterization of Historical leathers by thermal methods

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Keywords: historical leather, thermogravimetry/mass spectrometry, pyrolysis–gas chromatography/mass spectrometry,

Leather artefacts stored or displayed in historic buildings are vulnerable to changes in the outdoor environment due to the limited climate control. The protection of leather-based cultural heritage is a challenging task for the scientists and the researchers. Preservation of leather stability is the key to preserve the leather artefacts and their use values. However, preservation could be a difficult task because the conservation conditions of hundreds of years old leather-based artefacts are different in terms of one single piece of artefacts. The unknown tanning process and the conservation story of each artefact are additional elements that hinder conservation and possibly restoration. Understanding the degradation mechanisms and changes in the structure of leather could significantly help to find the proper way of protecting each artefact, to slow ageing and minimize the environmental negative effects and further damage.

The goal of the present paper is to obtain information about the composition and the structural stability of historical leathers, which can help to implement suitable conservation protocols. Nine historical leather samples were analyzed by thermogravimetry/mass spectrometry (TG/MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and micro differential scanning calorimetry (micro DSC). Micro-samples were taken from various artefacts (e.g. sword scabbard, travel chest, Cordovan upholstery, tobacco box and bookbindings from different periods) belonging to Romanian collections and dated between the XVII-XIX centuries. Few-year-old, vegetable tanned quebracho calf leather was used as a reference sample.

The applied micro-destructive thermoanalytical methods are suitable to characterize the chemical composition and structural stability of the historical leathers. The thermal stability and the decomposition profile of the samples were analyzed by the method of TG/MS, while the main decomposition products were identified by Py-GC/MS.

The TG study revealed that the maximum thermal decomposition rate of the historical samples is lower than that of the few-year-old vegetable tanned calf leather, most probably due to the slow degradation of the leather during the centuries. The concentration amount of the adsorbed water of the historical samples is higher that can be attributed to the degradation of the ancient tanning agents. The different ways of use of the artefacts are reflected in the different thermal stability of the leathers. The identification of the decomposition products allows characterizing the composition of the historical artefacts. We established that the yield of the decomposition products attributed to the vegetable tannins decreased in the chromatograms of the historical leathers. This result implies the degradation and the oxidation of the tanning agents over the centuries, which led to the deterioration of the leather-based artefacts.

The micro DSC study provided the extent of deterioration through destabilization, detanning and denaturation processes in historical leathers. The micro DSC approach enables a much more reliable evaluation of damage in historical leathers and a more refined relationship between the deterioration condition and the capability of historical leathers to extensively withstand environmental or man-made hazards.

Acknowledgments

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Energetic materials

Decomposition of hydrogen peroxide investigated with different calorimetric techniques

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Keywords: hydrogen peroxide, accelerating rate calorimetry, ARC, thermal hazard screening, thermal runaway

Pure hydrogen peroxide (H_2O_2) is a pale blue liquid, mixable in any ratio with water. Low-percentage aqueous solutions are widely used as bleaching agents due to their strong oxidizing properties. Besides for the bleaching of wood, paper or hair, hydrogen peroxide solutions are also used as oxidizing agents or in medical application as disinfectants. The tendency of hydrogen peroxide to decompose into water and oxygen is the reason for its application as a liquid propellant in rocket engines.

Accelerating Rate Calorimetry (ARC) is a method to study worst-case scenarios and thermal runaway reactions. In contrast to other caloric techniques such as reaction calorimetry, combustion calorimetry or Differential Scanning Calorimetry (DSC), ARC-type equipment allows for an adiabatic sample environment. Adiabaticity is essential in order to observe the most violent reaction progress possible. Decomposition reactions, which are of particular interest in this context, produce heat and pressure, since the reactions are usually strongly exothermic and are forming decomposition gases. The adiabatic sample environment is realized inside the ARC-type calorimeter via a set of heaters surrounding the sample compartment and via a smart temperature control regime. The first aim is to detect the temperature at which the self-decomposition of a sample or a sample mixture starts. And the second goal is to avoid any exchange of heat between the sample and the surrounding once the exothermic decomposition reaction has started. As soon as the self-heating rate exceeds a threshold (which is usually in the rage of 0.02 K/min), all heaters surrounding the sample will track the sample temperature. Without heat exchange, there will be no heat loss to the surrounding and if no heat dissipates, the entire heat of reaction remains inside the sample and increases the sample temperature. The higher the sample temperature, the faster is the rate of reaction. Such an experiment delivers not only the starting temperature of the decomposition reaction at quasi-isothermal conditions, it furthermore allows to determine the maximum temperature rise and the maximum pressure rise under adiabatic conditions. From both signals measured, temperature and pressure, the maximum rate can be calculated and predictions are usually made for the temperature at which the investigated reaction takes a minimum of twenty-four hours to reach its maximum temperature development rate, the time to maximum rate (TMR_{24h}).

This work presents results of the thermal decomposition of hydrogen peroxide solutions. A scanning device was used in order to detect whether or not the sample has a thermal hazard potential and an ARC-type device was employed in order to carry out test under adiabatic conditions.

Estimating RDX solubility in TNT at the melting point of RDX (198–204 °C)

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Keywords: RDX, TNT, solubility, DSC

The solubility of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in TNT (2,4,6-trinitrotoluene) at elevated temperatures is required to accurately predict the response of Comp-B (60:40 RDX:TNT) during an accident, such as fire. As the temperature increases, the TNT component melts, the RDX partially dissolves in the liquid TNT, and the remaining RDX melts (200 °C) as the Comp-B ignites. The solubility of RDX in TNT has only been measured up to temperatures of about 110 °C. In the current work, we used a differential scanning calorimeter (DSC) to estimate the solubility of RDX in TNT at the melting point of RDX. Most DSC measurements of Comp-B indicate that all of the TNT has melted before reaching 200 °C. The absence of an endotherm associated with the RDX melt has been interpreted as RDX being completely dissolved in TNT before reaching the melting point. We have observed that the endotherm is not absent, but is masked by exothermic reactions occurring at these elevated temperatures. We have inhibited the exothermic reactions by venting our DSC samples and measured the RDX melt endotherm in our Comp-B samples at about 200 °C. Using the measured heat flow associated with the RDX melt and published latent enthalpies of RDX melts, we have approximated the solubility of RDX in TNT to be 50-100 g_{RDX} per 100 g_{TNT}

Acknowledgments

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The potential of Biocarbon as CO_2 adsorbent in VPSA Unit

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Three processes are proposed for CO_2 capture from power plants, namely: the pre-combustion capture, oxy-fuel combustion and post-combustion capture (using either an absorption or adsorption method). Due to the large volumes of power plant flue gases, the possibility of using the adsorption processes, whose cycles are relatively slow, is limited. The structure of CO_2 adsorbents is crucial for the fast variable cycles needed for CO_2 capture from different punctual sources, such power plants. Activated biocarbons produced from biomass possesses high surface area and good thermal stability which makes them a highly attractive for CO_2 capture by adsorption methods [1-4]. In order to evaluate the possibility of using biocarbon for CO_2 adsorption in large-scale VPSA units, investigations of these compounds in laboratory are necessary. The main parameter of the evaluation of the potential of adsorbents to be used in VPSA plants still remains to be the sorption capacity, as expressed by the amount of adsorbed CO_2 per unit adsorbent mass. In the case of post-combustion CO_2 separation, the adsorbent must be appropriate for CO_2 capture from flue gas with the CO_2 content at a level of 10–15% under a total pressure of approx. 1-2 bar and at a temperature below 80^0C. The paper present the potential of biocarbon for CO_2 capture from coal fired power plant. The examination of the CO_2 sorption capacity and regeneration performance of biocarbon was carried out using a Mettler TGA/SDTA 851e thermobalance and TG-Vacuum system. The porous properties of the activated carbons were investigated by determining their nitrogen gas adsorption and desorption isotherms at –196°C, using an ASAP 2010 Instrument (Micromeritics). The specific surface area was calculated by the BET method. The FTIR spectra of the activated carbon was recorded at room temperature on a Nicolet 6700 spectrometer using KBr pellet technique. The microstructure of the biocarbon was made using a Electron Microscopes (EVO-40 Series, Carl Zeiss SMT) coupled with Energy Dispersive X-ray (SEM/EDX).

Acknowledgments

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Energetic performance and reaction mechanism of nano-aluminium based microspheres

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Keywords: nano-aluminum, Viton, thermal behavior, combustion performance

Nano-aluminum (nAl) particles with high reaction enthalpy have been widely researched for energetic system [1]. However, the surface chemical properties of nAl make it more sensitive to energy stimulate and easier to agglomerate after contacting each other during the preparation and storage process [2]. The surface passivation of nAl particles is effective method for safety and handling purposes as well as for its impact on thermal properties and energetic performance. Fluoropolymers have been used as passivating materials due to excellent chemical and thermal stability, which would also enhance the oxidation efficiency of nAl particles [3].

Considering additional energy and insensitivity provided by coating layer to formulations, the porous nAl@ Viton microspheres were fabricated utilizing the electrospray technology with polymers contents of 5, 10 and 15% by weight. The diameters of microspheres formed by tightly packed nAl particles and the different proportion of polymer were distributed mainly in the range of 3~5 µm. The thermal behavior of nAl@Viton microspheres were investigated by non-isothermal differential scanning calorimetry/ thermogravimetry/ mass spectrometry/ Fourier transform infrared spectroscopy coupling analysis. The result showed that the oxidation reaction mechanism of the microspheres was closer to nAl particles, which revealed a porous structure of the microspheres with nano features. The presence of fluoride ions inside the nAl particles influenced on the sintering mechanisms, and thus, allowed the control of the oxidation rate (Fig.1). Combustion tests suggested a faster propagation velocity rate for the microspheres despite possessing a reduced combustion heat compared with raw nAl. Viton layers provided multiple reaction pathways for nAl@Viton microspheres including fluorination, oxidation and carburization in the combustion experiments. The fire-resistant of Viton made the combustion performance of the nAl@Viton microspheres more dependent on the stimulation mode, so as to improve the thermal stability and environmental adaptability of the microspheres. The microspheres with the characteristic energetic performance stand on the positive side to play the advantages of nAl particles, and the polymers-contained microspheres have the potential to replace nAl particles as the propellant additives.

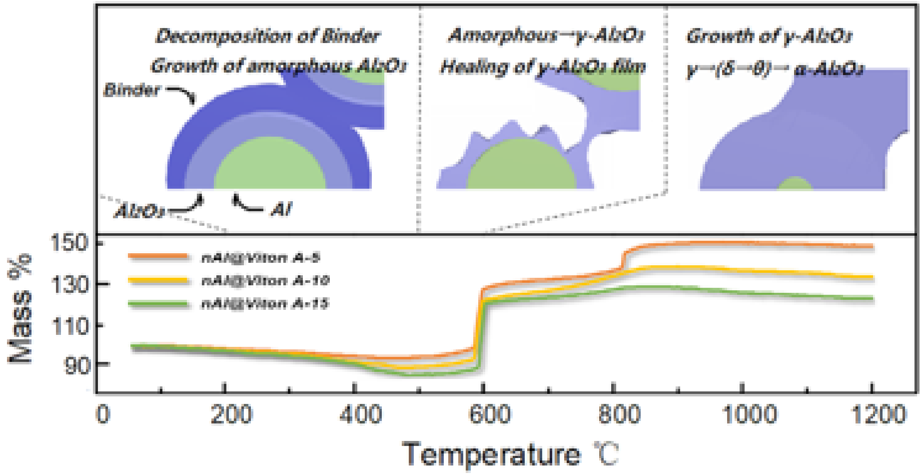

Fig.1 TG analysis of nAl@Viton-5/10/15 and the possible heating process of the electrosprayed microspheres.

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Thermal characterization of flash compositions containing potassium nitrate (KNO_3) and mg-al alloy

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Keywords: Pyrotechnic flash compositions, Differential Scanning Calorimetry (DSC), environmental friendly, potassium nitrate, Mg-Al alloy, Diversionary devices

Pyrotechnic flash compositions are generally employed for the production of light/sound in the military and fireworks applications. In general these are made with metallic fuels and inorganic oxidizers. Several researches are going on for replacing environmentally unfriendly pyrotechnic mixtures such mixtures containing barium nitrate ($Ba(NO_3)_2$) and potassium perchlorate ($KClO_4$) [1]. The pyrotechnic mixtures containing potassium nitrate (KNO_3) and Mg-Al can replace the mixtures containing barium nitrate ($Ba(NO_3)_2$), potassium perchlorate ($KClO_4$) and Mg-Al alloy. This study aims to understand the thermal characterization of pyrotechnic flash compositions containing potassium nitrate (KNO_3) and Mg-Al alloy by varying the weight ratios systemically. Thermal studies are carried out using the Differential Scanning Calorimetry (DSC). The onset temperature was found to be 445^{o}C for the composition containing 30% of potassium nitrate (KNO_3) and 70% of Mg-Al alloy. Thermal kinetics was also carried out using the Ozawa's kinetics method [2] and critical temperature for the thermal explosion [3] was also identified with the use of activation energy. The obtained thermal properties from this study were compared with the thermal properties of existing compositions to substitute the same. [4]

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A study on the ignition reaction kinetics and mechanism of B_4C/KNO_3 and $B_4C/KClO_4$ pyrotechnic smoke compositions

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Keywords: pyrotechnics, ignition reaction, kinetics, mechanism

Presented herein is a study on the ignition reaction kinetics and mechanism of B_4C/KNO_3 and $B_4C/KClO_4$ pyrotechnic smoke compositions using the non-isothermal thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. The pyrotechnics in oxygen balance of –10%, –20% and –30% were prepared for the experiments. The results of measurements show that the pyrotechnics in oxygen balance of –20% has the highest enthalpy. The activation energy (E_a) of ignition reactions were calculated by using Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) methods. The E_a values of B_4C/KNO_3 and $B_4C/KClO_4$ are 139.5 and 214.6 kJ/mol calculated by OFW method, 129.3 and 210.7 kJ/mol by KAS method. The differential and integral reaction mechanism functions of two compositions were determined by $z(\alpha)$ master plots method, $f(\alpha)$= 2(1-α)[-ln(1-α)]1/2 and $g(\alpha)$= [-ln(1-α)]1/2. The ln*A* values 11.6 and 22.3 min-1 were calculated by the intercept of KAS method. Also, XRD experiments were carried out on smoke particles, and the mass reduction showed by TG curves was analyzed, the most possible ignition reaction mechanisms were determined.

Acknowledgments
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Energy conversion and storage

In-situ real-time preliminary study of Carbon felt fibres interaction with LiBr, LiOH and Li4Br(OH)3 at microscale

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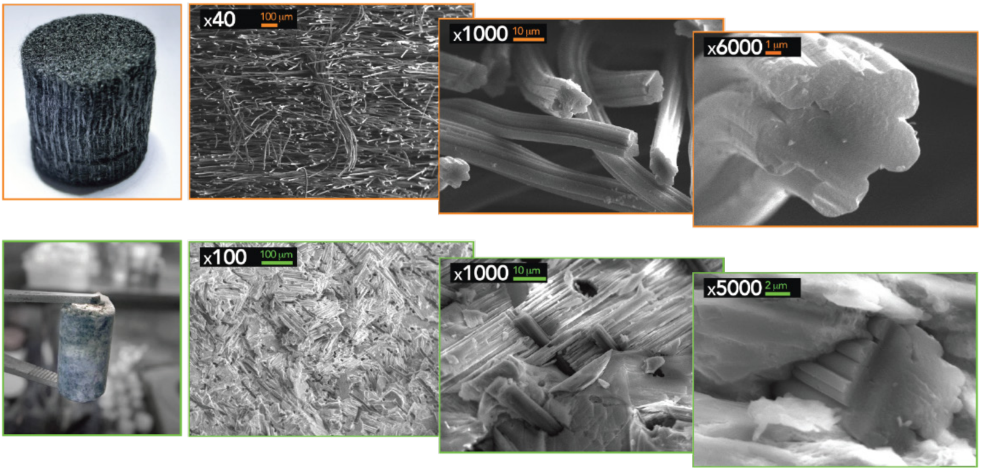
Keywords: Thermal Energy Storage; Hybrid material; High temperatures, Chemical compatibility

Graphical Abstract

Carbon felt before infiltration with $Li_4Br(OH)_3$



A theoretical search of advanced materials with high potential for cost-effective compact thermal energy storage at high temperature (300–600°C) has been performed [1]. LiBr/LiOH phase diagram at ambient pressure shows that $Li_4Br(OH)_3$ energy density is high (434 kWh/m^3) and that its working temperature (304°C) meets the requirements to potentially use it in solar thermal plants or in nuclear power plants with small modular reactors using thermal energy storage for instance (~300°C). The first thermal analyses confirm its high potential and led to the development of a hybrid material composed of $Li_4Br(OH)_3$ and of a Carbon felt to improve its stability and efficiency [2]. The operating conditions establishment fostering $Li_4Br(OH)_3$ formation process, under conditions close as much as possible to the chemical and thermal equilibria, requires the study of the Carbon fibres interaction with $Li_4Br(OH)_3$. To do so, the influence of working parameters (surrounding atmosphere nature, heating/cooling rates) is studied by using a hot stage placed inside the ESEM chamber. First, the compositions of carbon fibres, of the initial compounds LiBr and LiOH and of $Li_4Br(OH)_3$ are checked by using the X-ray powder diffraction technique. Then, their morphology evolution is monitored for different temperature protocols at each vacuum level in order to study the influence of carbon structures on $Li_4Br(OH)_3$ formation process. The first *in-situ* and real-time at microscale results are presented and discussed here.

Acknowledgments

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Thermal performance enhancement of beeswax/expanded graphite composite with eg/water suspension and Al_2O_3 based nanofluid

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Keywords: Thermal storage, Phase change material, Heat transfer fluid, Thermal conductivity, Latent heat

In this study thermal storage performance of beeswax as natural phase change material and its composite with expanded graphite (10 wt.%) was studied using three different types of heat transfer fluids i.e. plain water, expanded graphite/water suspension and alumina nanofluid. Heat transfer fluid of expanded graphite with water was prepared and tested at different concentrations (0.05 wt.%–1.0 wt.%) to enhance the heat transfer rate to phase change material. Similarly, alumina nanofluid was prepared at different concentrations (0.2 Vol. % –2.0 Vol. %) and used to charge the phase change materials. It was found that in case of both beeswax and composite of beeswax charging time decreased by 15.45% and 14.66% respectively with increase in concentration of EG/Water suspension upto 1 wt.%. Similarly charging time for pure beeswax and composite material was found to be reduced by 10% and 10.66% respectively with alumina concentration of 2.0 Vol. %. However, due to better thermal conductivity expanded graphite/water suspension showed lesser charging time as compare to the plain water and alumina nanofluid. It was also observed that composite of beeswax has been charged faster as compared to the pure beeswax when charged with each type of heat transfer fluid and found to be suitable for low temperature thermal storage.

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Experimental Investigation of Electronic Cooling using heat pipe and phase change material

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Keywords: Hybrid cooling, Electronic cooling, Heat pipe, Phase change material, Heat pipe assisted PCM

An experimental study is performed on cooling of electronic components like microprocessor using heat pipe (HP) along with phase change material (PCM). PCM possess high heat storage capacity and can maintain constant temperature during phase change. PCM absorbs the heat produced by microprocessor and transfer it to the evaporative section of HP which rejects the heat in to atmosphere, thus preventing the system from overheating and serious damage. Gravity assisted copper-water heat pipes are integrated into PCM (RT-54) and designed system is tested for 2h for four configurations under five different input loads ranging from 10W-30W. Results depicted that at load of 30W, the base temperature of heat sink containing PCM only, HP-PCM, HP-PCM with cooling fan decreased 36.3%, 43.5% and 60% as compared to empty heat sink.

Combi solar water heating and air source heat pump for space heating and domestic hot water application

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Keywords: solar thermal collector, solar water heating, air source heat pump, space heating, domestic hot water

In this research, the joint use of a solar water heating system and a heat pump for space heating and domestic hot water supply was investigated. An experimental prototype was developed and testing was carried out in the climatic conditions of the city of Almaty, Kazakhstan. A mathematical model and a numerical algorithm for calculating the energy efficiency and thermal productivity of the combined system based on the heat balance equation were developed. Also, a thermal analysis calculation was carried out separately for a flat plate solar collector and heat exchangers for a heat pump – evaporator and condenser. In the course of thermal analysis, data from temperature sensors and current weather data were taken as input. The analysis of the contribution of the solar water heating and heat pump parts to heat the water in the hot water storage tank was carried out. Both numerical analysis based on mathematical modeling and experimental analysis were conducted. The obtained data had a fairly good agreement and the efficiency of the heat pump COP varied between 2.5–3.5. As a recommendation from the study, conclusions were made about using this system at ambient temperatures not lower than –10 °C.

Acknowledgments

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Numerical simulation of heat discharge during solidification

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Keywords: undercooled phase change material, numerical simulation, heat transfer, discharge analysis

The SUDOKET project aims to map, consolidate and disseminate Key Enabling Technologies (KETs) for the innovative building sector. Nowadays, the energy demand is a major preoccupation and solutions must be found to optimize the the energy resources. Renewable energy resources will play a key role in meeting future energy demand. In buildings, one major challenge stands in the design of efficient energy storage systems to maintain energy use at a low level (i.e: low cost, high energy density, low ecological impact …). For last decades, there has been a growing interest in the development of systems based on phase change materials (PCM). PCMs for Thermal Energy Storage (TES) must be selected with drastic criteria to involve interesting properties. They must exhibit a large latent heat, a melting temperature lying within the operating practical range, they have to melt congruently with minimum subcooling and be chemically stable, low cost non-corrosive and non-toxic. Phase change materials (PCM) are very good candidates as a thermal energy material for seasonal cycles Regarding its properties, Xylitol has proven to be a promising candidate for Seasonal Energy Storage [1]. The purpose of this work is to estimate the thermal discharge behaviour of a xylitol rectangular sample while solidification occurs after subcooling state is over. Depending on the operating conditions, the discharge is more or less intense and long. Controlling these two aspects is of great help to enhance the thermal energy storage system.

A numerical analysis has been performed, based on a 2D rectangular xylitol sample. It is initially subcooled with an initial temperature Ti<Tm (Tm being the melting temperature). The boundary conditions are adiabatic, except on the right side where an exchange coefficient is applied to model the heat release. The home-made numerical code is based on finite volumes discretization. The energy equation is solved, with a source term to represent phase change, described through the Frenkel and Wilson equation that expresses the liquid-solid interface velocity against its temperature [2] and that shows that the interface has a maximum velocity for a defined critical temperature Tcrit<Tm. An iterative algorithm is computed to redistribute the source term in the whole domain in accordance with both temperature and solid fraction fields. The results have been given in terms of discharged heat against the Biot number Bi that expresses the competition between conduction in the sample and convection out of it, and against the Stefan number Ste that gives the competition between the sensible and the latent heats. The results show that during solidification, the released heat is submitted to an acceleration while the interface temperature increases from Ti to Tm, and deceleration when it overpasses Tcrit. The simulations show that increasing the Biot number accelerates the entire sample solidification and increases the maximal discharged heat. The study on the Stefan number proves that a critical value of Ste based on Tcrit leads to a maximal heat dis-

charge velocity and intensity. For a given Ste, the larger |Ste-Stecrit|, the slower solidification is, but the maximal heat discharge remains slightly at the same value for the considered Ste studied range

Acknowledgments

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Discharge of undercooled Xylitol-Erythritol eutectic blend for Seasonal Energy Storage

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Keywords: Thermal Energy Storage, Undercooling, Activation and Crystallization, eutectic Xylitol-Erythritol blend

SUDOKET project aims at mapping, consolidating and disseminating Key Enabling Technologies (KETs) for the innovative building sector. Thermal energy storage (TES) is one of the key elements to optimize the use of available energy resources (especially renewable ones) and to improve the energy efficiency of buildings. Phase change materials (PCMs) used for TES are an important class of materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. In this framework, our objective is to study biosourced phase change materials, able to compete with water as storage material and presenting improved performances in comparison with currently used PCMs. An ideal PCM for this application must have a melting temperature inferior to 100°C, a high energy density (> 100 kWh.m^{-3}) for the compactness of the storage system and a large undercooling in order to limit heat losses over the long term storage. The energy is stored in undercooled melts and when heating is needed, the storage system is discharged by activating the PCM's crystallization. The subsequent discharge power depends on its crystal growth kinetics.

Among bio-based materials, the eutectic Xylitol-Erythritol blend initially investigated in the framework of the FP7 EU SAM.SSA Project has a high potential as a TES material [1]. It is composed of 64%mol of Erythritol and 36%mol of Xylitol and is referred as Xy-Ery$_{(eu)}$ thereafter. Its melting point is inferior to 100°C which allows combining the storage unit containing Xy-Ery$_{(eu)}$ with cheap solar collectors. Its latent heat is superior to 250 J.g^{-1} and its total energy density is 4-5 times higher than the one of water (110-150 kWh.m^{-3} whereas it is approximately 30 kWh.m^{-3} for water on a seasonal basis). Its high and stable undercooling allows long-term storage in a metastable state with reduced thermal losses and a negligible risk of spontaneous discharge. Its cost is acceptable (< 3 €/kg) and it is widely available in the market.

In this work, Xy-Ery$_{(eu)}$ thermo-physical properties are first recalled [2]. Two series of experiments, both combined with numerical data processing, are presented: one on the activation of the discharge process and the other one on the crystal growth kinetics. The first series consists in applying an efficient and low-cost technique, successfully tested for undercooled Xylitol activation [3], on undercooled Xy-Ery$_{(eu)}$ melts at different undercooling degrees. The second series aims at measuring crystal growth rates in undercooled melts of Xy-Ery$_{(eu)}$ according to the undercooling degree. The obtained crystal morphologies are also observed and discussed in this study. It has been shown that for a storage system containing Xy-Ery$_{(eu)}$, the activation of the energy discharge process (crystallization activation) is difficult and the subsequent crystallization rates (discharge powers) are very low. Indeed, it was observed that bubbling fails in crystallizing the melt for initial temperatures inferior to 55°C, which is far from ambient temperature. Another solution consisting in adding a solvent-antisolvent system to a Xy-Ery$_{(eu)}$ blend in order to achieve crystallization at temperatures inferior to 55°C is finally considered.

Acknowledgments

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Estimations of Thermal conductivity and thermal diffusivity of phase change materials in solid and liquid phases

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Keywords: Thermal conductivity, Phase Change Materials, Solid and liquid phases

According to European commission for energy, building sector represents presently 40% of energy consumption and 36% of CO2 emission in Europe [1]. Thermal energy storage is thus seen as a key step to optimize the use of available energy resources (especially renewable ones) and to improve the energy efficiency of buildings. Phase change materials (PCMs) considered for the thermal energy storage are an important class of materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. In this framework, our objective is to develop and study new biosourced phase change materials, that can be incorporated to buildings walls and that present improved performances in comparison with currently used PCMs (i.e.: low cost, high energy density, low ecological impact…). Even if their melting point and latent heat of fusion estimations are of great interest, other criteria such as specific heat, thermal conductivity, thermal diffusivity, density and viscosity as a function of the temperature are necessary for modelling and/or for proper material comparisons of PCMs performances.

In this work, we present the methods developed to assess the thermal conductivity and the thermal diffusivity evolutions with temperature of a few biosourced PCMs. This means the estimations are performed for both liquid and solid phases. A transient HotDisk like method has been developed to assess the PCM thermal conductivity and thermal diffusivity in solid state. The device consists of a heat source, providing a homogeneous heat flow, inserted between two cylindrical solid samples and a thermal flux sensor allowing the measurements. A transient method using a hot cartridge has been developed to assess the same properties in liquid state this time [2]. The PCM at liquid state fills the gap between a glass tube and the hot cartridge placed inside it. The liquid thickness has to be such as the convection phenomena are avoided. Three thermocouples are appropriately placed to monitor the temperature evolution of the liquid phase.

The power supplies as well as the thermal flux control of both benches have been remoted by an Arduino-based electronic device. Inverse methods have been applied to the obtained signal recorded by the thermocouples to estimate the thermal conductivities and thermal diffusivities with temperature for each studied PCM.

After validating both of these methods, the obtained results are presented and discussed in this work.

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Reversible carbonation and decarbonation reactions for large scale CO_2 capture and thermochemical energy storage

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Keywords: Reaction Looping, Thermochemical Energy Storage, CaO, CO_2 Capture, Reaction Kinetics

The multicycle carbonation/calcination of CaO, also known as calcium looping (CaL) has been demonstrated as a feasible technology for reducing CO_2 emissions in fossil fuel power plants at low cost. In this process, the CO_2 released with the flue gas stream from the power plant reacts with CaO particles in a carbonator reactor at temperatures of about 650ºC and a CO_2 concentration of about 15%. Under such favourable conditions, the carbonation reaction takes place very rapidly and the evolved gases from the carbonator are almost CO_2 free. In order to regenerate the CaO sorbent for subsequent carbonation reactions, the $CaCO_3$ produced in the carbonator is circulated into a calciner reactor at a temperature of about 900ºC. The concentrated steam of CO_2 released out of the calciner is ready for storage or reutilization in another application such as oil enhanced recovery or chemicals production. More recently, CaL has also been proposed as a thermochemical energy storage system in concentrated solar power plants (CSP-CaL). In this way, solar radiation is employed to drive the endothermic decarbonation reaction at high temperatures. The chemical energy stored in the reaction products; CO_2 and CaO can be recovered by inducing the exothermic carbonation reaction thereby producing electricity on demand even after sunset. In this way, the intermittent nature of solar energy can be overcome.

The reliable estimation of the kinetics driving both carbonation and calcination reactions is of fundamental importance for modeling the process and designing the plant. For instance, the minimum required residence times for significant carbonation are quite relevant as short residence times are a must for CaL to be efficient. An important drawback of this technology is related with the sintering-induced deactivation of CaO with the number of cycles that requires of frequent make up of fresh sorbent. Such deactivation is a consequence of significant reduction in the active surface available for fast carbonation but also due to the formation of a blocking calcium carbonate layer on the particles surface when the carbonation reaction is carried out at high temperatures. The working conditions for carbonation and calcination are constrained by the application and by the composition of the flue gas stream. Thus, to improve the performance of the sorbents some strategies have been proposed such as the use of thermal or mechanical pretreatments or the employment of inert additives such as nanosilica, alumina or zirconia to act as a hindering agent for sintering. Alternatively, the use of dolomite instead of limestone shows great promise as the nanometric grains of MgO produced after dolomite appear homogeneously dispersed and are able to maintain the sorbent stability during a much larger number of cycles.

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Investigating the heat transfer of organic phase change materails enhanced with nanoparticles

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Keywords: phase change material, nanoparticle, convective heat transfer, thermal conductivity

Latent heat storage systems are very useful since they are able to store considerable amounts of energy for smaller temperature differences. This is due to the constant temperature of the melting/solidification process, while still large heat values are exchanged. Phase change materials (PCMs) are substances that are used within these system types. In certain heating/cooling applications, the rate of heat storage/rejection is of critical importance, including vehicle battery applications, building applications, and others requiring heat transfer across shorter time intervals. Therefore, the response time of a heat storage unit becomes an important design parameter, which plays a role in determining the system's technical and economic efficiency. Among various PCM types, organic PCMs, namely Paraffin waxes and fatty acids, are more widely utilized in latent heat storage systems due to congruent melting and stability. However, they commonly suffer from lower thermal conductivities, making their response time inappropriate for a wide range of industrial and technical applications. A rather novel method to increase the thermal conductivity of organic PCMs is dispersion of nanoparticles. Several metallic, metallic oxide and carbon-based nanoparticles could be added in various amounts to increase the system response time.

In this paper, the heat transfer behaviour of an organic PCM, enhanced with added nanoparticles, is numerically modelled and studied. The PCM is assumed to be Paraffin and multiple metallic and metallic oxide nanoparticles are considered as the heat transfer enhancers. For the heat transfer behaviour, the conductivity coefficient as well as the latent heat of fusion of the nano-enhanced PCM (NEPCM) is specifically studied. Furthermore, the effect of nanoparticle on the convective heat transfer within the liquid phase of the PCM during the melting period is investigated. It is apparent that certain nanoparticles increase the heat transfer rate, and therefore, enhance the storage response time, making PCM utilization more effective in the applications dependant on faster heat transfer response times. In this regard, metallic nanoparticles are proved to be more effective on the thermal conductivity enhancement. Finally, for the optimum nanoparticle, the correlations relating the heat transfer characteristics with the physical parameters of the nanoparticles, namely nanoparticle weight percentage as well as nanoparticle diameter, are developed.

Effect of salt addition on methene emissions during storage of pig slurry and subsequent biogas production

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Keywords: pig slurry, methane emissions, biogas production, salt addition

Pig slurry (PS) is often held in the liquid form in the farm, waiting for transporting to the final treatment facilities. This storage period lasts for, in general, 1-3 months, in which huge amount of methane (CH4) can be emitted by the activity of indigenous microbial consortium. To reduce this CH4 emission, acidification by using sulphuric acid and lowering temperature below 15oC are currently applied [1-2]. However, the acidification has the hazards associated with this strong acid, and the increased presence of hydrogen sulfide in the subsequent biogasification process [3]. And, the decrease of temperature at a high degree seems unrealistic, requiring huge additional energy input, and thermally-isolated cover structure.

In the present work, the new method was tested that adding salt to PS. Salt is easily attainable at a cheap price, and is known to inhibit microbial activity by increasing osmotic pressure. Salt was added to PS to reach the concentration from 1 to 13 g Na+/L, and then stored at 30oC for 40 d. As storage went on, a cumulative amount of CH4 emissions was increased, finally recording 8.8 kg CO2 eq./ton PS, in case of control. However, in salt added cases, it dropped gradually with increasing salt concentration, from 8.3 to 2.9 kg CO2 eq./ton PS, with less degradation of organic matters. In case of control, organic content was degraded by 40% while it was only 20% at 7 g Na+/L. Instead of using salt, brackish wastewater (BWW) from desalination plant was also tested. It was found that BWW was more effective in reducing CH4 emissions, ascribed to the presence of other inhibiting components like heavy metals. The CH4 emissions was almost dropped by 50% at 5 g Na+/L. The stored PS was then tested for biogas production. The control sample showed a biological methane potential of 148 mL CH4/L PS, while the sample stored at 7 g Na+/L showed 171 mL CH4/L PS. By reducing CH4 emissions during storage and increasing the amount of biogas, it can be concluded that salt addition to PS can reduce overall greenhouse gas emissions by 6-54%.

Experimental techniques

For PS storage experiment, a cylindrical tank with a total volume of 1.4 L was used. One litre of PS was added, beside NaCl doses to reach concentrations of 1-13 g Na+/L. On the other hand, certain amounts of brackish wastewater were also tested through being added to 0.8 L of PS to reach final concentrations of 1-9 g Na+/L. Volumes were then adjusted to reach 1 L using distilled water. All tanks were purged with fresh air in order to provide actual storage conditions. Temperature was kept at 30±1 oC using water bath.

For biological methane potential experiments, bottles of 0.6 L working volume were used in continuous mode, while hydraulic retention time (HRT) was fixed to 30 d, corresponding to 2.0-2.8 g COD/L/d of organic loading rate (OLR). Temperature was kept at 37±1 oC, while the agitation speed was 120 rpm.

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Effect of radiation on MHD time-dependent Casson fluid flow past an exponentially stretching curved sheet

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This paper presents the flow and heat transfer attributes on unsteady flow of an electrically conducting Casson fluid past an exponentially stretching curved sheet. The fluid motion is assumed to be laminar and time-dependent. The effects of temperature-dependent thermal conductivity, Joule heating, radiation, and variable heat source/sink are deemed. Suitable transformations are pondered to alter the governing PDEs as ODEs and then elucidated by the numerical procedures like Shooting and Runge-Kutta method. Graphs are outlined to describe the influence of diverse flow parameters on the fields of velocity and temperature. We observe that there is an enhancement in the field of temperature with the radiation, temperature-dependent thermal conductivity and irregular hear parameters. Also, the Casson parameter has a tendency to suppress the distribution of momentum but an inverse development is noticed for the curvature parameter. Attained outcomes are also equated.

Thermal degradation kinetics of the spent adsorbent

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The use of low-cost adsorbents for the treatment of various wastewaters generates large volumes of solid waste. These solid wastes have great potential for energy recovery. These aspects are being studied separately in our laboratory by other researchers and, therefore, are included in this work. The dried acrylic acid (AA)-loaded spent powder activated carbon (PAC) can be regenerated by desorption either with methanol or by thermal means. PAC cannot be fired, as it is very costly. Hence it is to be regenerated and reused. The AA-loaded adsorbent was studied for their thermal degradation characteristics by thermo-gravimetric (TG) instrument. The degradation kinetics of these adsorbent was studied using different kinetic models.

Amplifying the enthalpy of form-stable phase change materials bearing methyl red group with UV light

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Keywords: phase change material, methyl red, UV light

For conventional form-stable phase change materials (FSPCMs), the phase change enthalpy was fixed once the materials were constructed. In present work, methyl red functioned polyurethane-based FSPCMs were synthesized and irradiated with UV light. DSC analysis results showed that the enthalpy of the activated FSPCMs with UV was amplified compared with the unactivated ones. UV light treatment can promote the crystallization of the soft segment in polyurethane, which can be proved by XRD measurement. Furthermore, irradiating the activated films with visible light can cause reverse effect that the enthalpy and crystallization get back to the original degree. FTIR, DMA, TG were also performed to determine the structure and properties of the FSPCMs.

Phase change materials based on recycleable thermosetting polymers for thermal energy storage

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Keywords: phase change materials, thermal energy storage, thermosetting polymers, recyclable

Phase change materials (PCMs) for renewable thermal energy storage are beneficial to solve energy crisis and environmental deterioration. Particularly, PCM based on polymers have drawn extensive attraction due to their superior properties. Thermosetting polymers can provide reliable restrict effect and robust mechanical properties, while thermoplastic polymers are capable of giving PCMs excellent recyclability and reprocessability. Here we report an economical feasible, facile, eco-friendly method with a dynamic crosslinks for thermosetting PCM to obtain both good thermal storage capacity and recyclability. Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical composition of SSPCMs. Xray diffraction (XRD) and Polarizing optical microscopy (POM) were adopted to compare the crystalline properties of PCMs. Differential scanning calorimetry (DSC) was conducted to investigate the phase change properties before and after reprocessing. Thermogravimetric analysis (TG) was carried out to reveal the thermal reliability.

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Self-luminous polyethylene glycol based phase change materials for both thermal and light energy storage

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Keywords: Self-luminous; Phase change materials; Thermal energy storage; Light energy storage

Phase change materials with high efficient energy storage for thermal energy and light energy are of critical importance in sustainable development, which have been broadly applied in the field to reduce energy consumption. In this work, a novel self-luminous material integrated the long lasting phosphors into polyethylene glycol based phase change materials (PCMs) with superior thermal energy storage and excellent light energy storage is reported. The synthesized self-luminous polyethylene glycol based PCMs shows high latent heats, excellent thermal reliability and thermal stability from differential scanning calorimeter (DSC) analysis, the thermal cycling test and thermogravimetric (TG) analysis. Importantly, self-luminous polyethylene glycol based PCMs can absorb ultraviolet and visible light from lighting source and natural light yet emit various colors of light in the dark for many hours by the addition of various long lasting phosphors. This results demonstrate self-luminous polyethylene glycol based PCMs can store both thermal energy and light energy, showing great potential in applications including emergency light, indication sign, storage and building energy conservation.

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Thermal characterisation of building components having pcm layers

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Keywords: Phase change material (PCM), thermal energy storage, building components, numerical modelling , thermalperformance

The Building sector is one of the larger energy consumers than needs to ensure a significant decrease up to year 2050. Several thermal and energy performing solutions are required to be employed at buildings, in order to obtain the required reduction. The paper analyses the implementation of Phase Change Material (PCM), in components of the building envelope. The aim of using a PCM is that of enhancing the thermal storage capacity (i.e. thermal inertia) of the building components. Thus, first a numerical study of the melting process of a PCM in a differentially heated rectangular cavity is done. Simulations are carried out with the commercial software ANSYS-Fluent. It is found that the melting rate of PCM is dominated by conduction. The heat transfer by convection decelerates the movement of the solid-liquid interface because the PCM melting is concentrated only in the upper part of the cavity. Second, several solutions for incorporating PCM in building components are modelled and analysed. The focus is set on five climatic zones, dominated by temperatures ranging from –12°C to –24°C. For the interior boundary conditions, variation between +18°C up to +24°C, and a variation for the relative humidity value from 25% up to 8%, are considered. The conclusions are drawn based on the way that the thermal performance varies along with the boundary conditions for the two sets of buildings components, respectively without PCM and with PCM.

Acknowledgments

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Experimental investigation on oxidation stability of pyrolyzed annona squamosa seed cake oil using tea leaves extract as an anti-oxidant

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Conventional fossil fuels are getting depleted due to its large consumption worldwide, this creates the need for alternate fuel. Numerous research programs are currently underway to introduce bio-fuel as a substitute for fossil fuels. At present, pyrolysis oil is used as a blend along with diesel but the usage of pyrolysis oil along with diesel as a fuel in the engine is highly tedious because of its unstable nature. This project is focused on improving the stability of pyrolysis oil by adding tea leaves extract as a natural anti-oxidant. For the production of pyrolysis oil, the seed cake of Annona Squamosa used as a new feedstock. The TGA test was conducted for the feed-stock to find the yield point temperature. Proximate analysis was carried out for testing the suitability of pyrolysis. As per the TGA results, pyrolysis process is conducted at the temperature range of 450–550°C. The bio-oil is characterized by means of various physical property tests. FTIR test is used to verify the functional groups of both the raw pyrolysis oil and the antioxidant added pyrolysis oil and then Rancimat analyser is used to analyse the oxidation stability of the pyrolysis oil. The oxidation stability index of pyrolysis oil is found to be improved from 0.52 hour to 4.33 hour after adding antioxidant, which is in accordance with ASTM (D6751).

Carbon footprint and economic analysis of fuel cell assisted road transport refrigeration system

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Keywords: Solid oxide fuel cell, SOFC, Absorption refrigeration, Sustainable Road Transport Refrigeration, Greenhouse Gas Emissions

In Europe today, more than a million transport refrigeration units (TRU) are in operation using vapour compression refrigeration technology powered by diesel engines. They produce significant greenhouse gas (GHG) and particulate matter (PM) emissions [1] at the same time not being covered by any environmental regulation. Concerns over the carbon footprint of TRU have increased the need to design and develop alternative clean refrigeration technology. With the increased interest in employing fuel cell technologies in the automotive industry, there is an opportunity to utilise heat generated by solid oxide fuel cells (SOFCs) to supply the required energy to vapour absorption refrigeration systems (VARS) for refrigeration.

To examine this concept further, the present study examines the feasibility of SOFC assisted VARS for refrigerated transport to replace the conventional TRU, where the heat generated from SOFC can be used to run the VARS. The study investigates and compares the GHG emissions from SOFC assisted VARS, diesel, and natural gas (NG) engine powered TRU, and cryogenic transport refrigeration systems. The operational and production related emissions were considered here to find out the total GHG emissions from the above mentioned systems. Hydrogen fuelled SOFC was considered in this work, and four different hydrogen (H2) production methods (solar based electrolysis, wind based electrolysis, biomass gasification, and NG reforming) were studied to calculate the hydrogen production related emissions. The analysis was then applied to systems for chilled and frozen products over a 10 hour vehicle operation. Finally, to select an optimum system configuration, both environmental and economic aspects were be considered. Therefore, a single key performance was determined, and evaluated for different system configurations.

The mass intensity of the various fuels to obtain the required amount of refrigeration load in the different systems was calculated. It was found that SOFC-VARS required the least amount of fuel (2 to 7 kg of H2) while the fuel mass intensity of cryogenic refrigeration systems was the highest (up to 540 kg of Liquid Nitrogen and Liquid Carbon dioxide) while the amount of diesel and natural gas required for conventional TRUs varied from 15 to 35 kg and 12 to 30 kg, respectively. The result showed that the considered novel SOFC-VARS emitted considerably lower amounts of GHG (50–75 % reduction) compared to diesel and natural gas (NG) fuelled TRUs, and cryogenic transport refrigeration systems. It is interesting to note that the GHG emission from SOFC-VARS greatly depends upon the hydrogen production method. Wind based H2 production emitted the least amount of GHG (0.001 to 0.006 gCO2e/kg-km) followed by solar based production (0.002 to 0.01 gCO2e/kg-km), biomass gasification (0.005 to 0.02 gCO2e/kg-km), and NG reforming (0.01 to 0.07 gCO2e/kg-km). The fuel production cost associated with the different systems was also evaluated. As NG reforming is the main current H2 production method, it depicted the lowest production cost followed by biomass gasification, wind electrolysis, and solar electrolysis.

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Influence of temperature on properties of selected materials for energy storage and conversion applications

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Keywords: protonic conductors, Al-ion batteries, supercapacitors, optimization of preparation method, composite materials, chemical stability, temperature dependent properties

The aim of this work was to compare the selected properties of different simple and complex metal oxides, such as V2O, WO3, ZnO, SnO2, and perovskites of the general formula ABO3, in particular, BaCe0.9Y0.1O3. The common feature of these materials is that they are widely considered for applications in the construction of electrochemical devices for energy conversion and storage, such as solid-oxide fuel cells, metal-ion electrochemical batteries or supercapacitors. The developed materials should exhibit the specific properties, depending on the function in the manufactured electrochemical device.

In the case of protonic solid-oxide fuel cells the optimized perovskites, in particular, BaCe0.9Y0.1O3, are used as the solid electrolyte, due to relatively high proton conductivity at high temperatures [1-2]. The optimization of these materials is focused on an increase of protonic conductivity and improvement of chemical stability especially in atmospheres containing CO2 and H2O. The improvement, in this case, can be done by preparation of composite materials, where additional phases are introduced into intergranular (grain boundary) regions.

In the case of metal-ion batteries, such as well-known Li-ion or currently developed Al-ion batteries, the proper selection of cathode and anode materials leads to the improvement of electrochemical performance of materials. Different simple oxides such as V2O, WO3, ZnO, were tested and the correlations between crystal structure, microstructure, electronic properties and the performance of constructed prototype Al-ion batteries was investigated. The improvement of the performance was achieved by the preparation of composite metal oxide – carbon structures, by using the sol-gel route and the controlled thermal treatment of obtained precursors.

In the case of supercapacitors, the mechanism of operation of such devices is based on storing electric energy in an electrochemical double layer, forming the solid-electrolyte interface. The use of nanomaterials, highly porous structures and composites of metal oxides with carbon currently leads to the best results from the point of view of performance optimization. The influence of the defect structure of SnO2 on properties of manufactured supercapacitors was investigated in our work. The SnO2 with different concentration of oxygen vacancies was obtained during controlled heat treatment in given gas atmospheres.

In our current works, the optimized materials were characterized using the Scanning Electron Microscopy, Differential Thermal Analysis and Thermogravimetry coupled with Mass Spectrometry, X-ray Diffraction method, Raman spectroscopy, and Electrochemical Impedance Spectroscopy technique. The influence of heat treatment conditions during the preparation of materials and the dependence of temperature on properties of materials were analyzed and discussed from the point of view of improvement of performance of constructed electrochemical devices.

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Valorisation of food wastes through torrefaction – thermal decomposition and kinetic analysis

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Keywords: combustion, pyrolysis, parallel reactions, heating value

Due to the growing generation of urban organic waste worldwide, which is mainly constituted by food waste, it is necessary to explore alternatives to take advantage of these, in order to reduce the environmental impact caused by them. Therefore, the aim of this work was to investigate the torrefaction of a lab-prepared food waste sample as a process for the valorisation of this biomass.

The food waste samples were cooked in the lab facilities by using steam for 1 hour. The torrefaction process was carried out in a muffle furnace (Terrigeno, Model D8, Colombia) after drying, using closed petri dishes in order to simulate a reducing atmosphere. The analysed temperatures were 150, 225, and 300 °C, using residence times of 15, 30, and 60 min. Then, the torrefied samples were characterised by determining the contents of moisture, volatile matter, ash and fixed carbon. Also, the heating value was determined by means of a bomb calorimeter (Parr, model 6200, USA). In order to analyse the torrefaction process, as well as the combustion reaction kinetics of the torrefied samples, was selected the torrefaction condition (temperature and time) which presented the more representative heating value. Afterwards, by using a thermogravimetric balance (TA Instruments, model TG 5500, England), were carried out non-isothermal experiments in atmosphere of synthetic air at the heating rates of 2.5, 5, and 10 °C/min. Also, in the thermogravimetric balance were performed isothermal experiments at the temperatures of 250, 300, and 350 °C with a residence time of two hours, in order to investigate the torrefaction process. The combustion kinetic analysis applied was based on a reaction mechanism of six parallel reactions according to previous works [1].

The results of the characterisation showed moisture content in the food mixture of 74.2%. About the proximate analysis, the results in dry mass basis was 80.77% volatile mater, 2.27% ash content, and fixed carbon of 16.94%. Also, through ultimate analysis was determined a composition of 47.6% carbon, 5.9% hydrogen and 43.6% oxygen. These results were according to the literature [1].

The selection of the better torrefaction conditions was through a comparison of the heating value of each condition with the dry sample. Then, the higher heating values registered were 18.70, 17.19, 18.21 MJ/kg for 150 °C and 15, 30, and 45 min, respectively. For 225 °C and 300 °C and the same times were 19.68, 18.75, 18.19 MJ/kg, and 23.96, 26.20, 26.25 MJ/kg, respectively. The heating value of the dry sample was 18.30 MJ/kg. Then, the better energetic condition was achieved at the temperature of 300 °C and 30 min.

The combustion kinetics of the torrefied biomass was characterised by six independent parallel reactions, which activation energies were 200, 204, 49, 130, 180, and 130 kJ/mol, respectively. The pre-exponential factors related to each of the six reactions were 9.95×1015 s-1, 1.66×1015 s-1, 2.00×101 s-1, 3.15×107 s-1, 1.27×1010 s-1, 2.50×105 s-1, respectively.

The reaction model for each of the six reaction was the same, first order reaction. The error involved in the model prediction was measured and kept lower than 3%. Finally, it was concluded that the food residues, e.g., restaurant residues, could be a good and cheap raw material for energetic purposes, since its combustion after thermal processing will release sufficient energy for the torrefaction process and for other uses, e.g. steam generation, or simply as a heat source.

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Modeling and multi-objective pareto optimization of PCM melting process in a finned enclosure using CFD, ANNS and NSGA-II algorithm

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Keywords: Phase change materials, Thermal energy storage, Multi-objective optimization, Finned enclosure, GMDH type neural networks

Latent heat thermal energy storage (LHTES) systems have many applications in a variety of engineering fields such as heat recovery devices, heating and cooling of buildings, thermal storage of solar energy, electronic cooling and so on. The main issue in LHTES systems is to store the maximum amount of energy in the possible shortest time. In this study, an attempt was made to provide optimal configurations of a finned enclosure in phase change material (PCM) melting process. According to the considered design parameters such as dimensionless length of fins, number and volume fraction of fins, a multi-objective optimization has been used with the objective of achieving the highest thermal energy storage inside the enclosure in a minimum period (time interval). For this purpose, a computational fluid dynamics (CFD) was used to simulate the melting process of PCM in a finned enclosure. The aim of the CFD simulation was to investigate how the input variables influence the energy storage and storage time. Then, using a group method of data handling (GMDH) type neural networks, two models were extracted that relate the objective functions to input variables. In the next step, the obtained models were used along NSGA-II to obtain the Pareto optimal solutions. It is confirmed that the obtained Pareto optimal points involve significant design information on finned PCM enclosure.

Numerical study of nano-PCMs FOR energy storage improvement

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Keywords: Energy storage, Phase Change Material, nanoparticles, numerical simulation

The development of energy storage devices is crucial nowadays and represents an important area for innovation. During the last decade, energy storage has been improved with the use of phase-change materials, PCM [1]. The PCMs commonly used in industrial applications are based on paraffin, barium chloride, oleic acid and stearic acid depending on the targeted temperature range. The paraffin wax is one of the most promising since it possesses many desirable characteristics: non-corrosive, chemically and thermally stable and its phase change temperature can be adjusted. However, paraffin wax is characterized by a very low thermal conductivity and a large volume change during the melting process. The recent advances in the field of nanotechnology gave rise to a new class of nanometeric metallic and non-metallic particles characterized by their substantially higher thermal conductivities. These particles, referred as nanoparticles, are dispersed into a conventional fluid, creating a new class of heat transfer fluids named nanofluids [2]. Nanofluids have shown their ability to enhance the heat transfer performances of the host fluid, which constitutes a great potential to increase the energetic efficiency of thermal systems [3, 4]. Recent research showed that adding nanoparticles to PCMs improved remarkably the heat storage capacity. Therefore, a promising new class of phase change materials, called nano-PCMs is widely investigated [5, 6]. In this context the main objective of the present paper is to numerically study the thermal behavior and the heat transfer characteristics of Paraffin RT50 as PCM during constrained melting and solidification processes inside a shell tube heat exchanger. In addition, the potential for improving the thermal properties of PCMs, such as thermal conductivity, specific heat and latent heat, will be explored by adding nanoparticles. Different nano-PCMs will be tested by mixing paraffin RT50 with different types of nanoparticles, such as alumina, copper, copper oxide, silicon dioxide and also titanium dioxide under different temperature ranges. The geometry corresponds to the experimental set-up developed by Hosseini et al. [7]. It consists of a horizontal shell tube heat exchanger of 1 m length, outer and inner diameters equal to 0.088 m and 0.022 m, respectively. The enthalpy-porosity method is used in order to model the phase change of melting and solidification in the heat exchanger. In addition, the single-phase model is assumed to simulate the nano-PCMs. The effects of the operating temperature, nanoparticle concentrations, ranging from 0 to 4 vol.%, and nanoparticles type on the stored energy are investigated.

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Integrated treatment of bio-wastes for circular economy

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Keywords: bio-carbon, agricultural and industrial bio-wastes, sludge from bio-treatment waste waters, thermal and radiation treatment technologies

Review on the methods and technologies for integrated treatment of bio-wastes oriented to the utilization and recycling of Carbon and improve energy efficiency are the main subject of presented paper. Recycling of Carbon is essential for Agriculture and soil productivity and it is aa important for Sustainable Carbon Life Cycle. The same time it is well known that all bio-wastes generated have a heat capacity and it is a matter of the method and technology selection to be used efficiently for heat and electricity production. As the results from the practice and investigations have shown the pretreatment drying process could be effective if only cheaper solar energy or heat of waste gases is utilized. In some case radiation pretreatment is also needed on the way to avoid harmful pathogens and hazardous substances as impurities.

On the base of data available and obtained from out investigations it was found that it is essential to obtained final products with water content less than 10wt%. This is the way to avoid bad smell released and to make bio-waste free from pathogen microorganisms. It was confirmed that all products obtained are free from pathogen microorganisms and different weed seeds, affecting the yield and soil sustainability.

The processes and optimal conditions determined are recommended for practical use and some of them are recommended as a good and sustainable practice successfully.

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Features of the mechanosynthesis of proton-conducting molybdates R10Mo2O21 (R = La, Nd, Y, Er) containing magnetic (r = Nd, Er) and non-magnetic cations (R = La, Y)

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Keywords: rhombohedral phase, bixbyite, mechanosynthesis, proton conductivity, electronic conductivity

LnZrMoO (Ln= La, Nd, Sm, Dy, Ho) Zr-doped molybdates, $La_{5.5}MoO_{11.25}$, $Nd_{10}Mo_2O_{21}$ have mixed electron–ion (electron–proton) conductivity and are promising materials for SOFC electrolytes and proton-conducting membranes[1-3]. Zirconium doping improves the stability of these materials to reduction, but it also decreases their conductivity by about one order of magnitude.

In this work, we use XRD, ESR and DTA/TG in combination with mass spectrometric analysis of the gas released during heating at 10°C/min to 1200°C in oxygen or helium containing 0.1% oxygen to study reactions underlying the mechanochemical synthesis of $R_{10}Mo_2O_{21}$ (R = La, Nd, Y, Er) molybdates from R_2O_3 and MoO_3 at room temperature.

The major phase resulting from the mechanochemical synthesis is a cubic phase with the bixbyite structure ($Ia\bar{3}$) for $R_{10}Mo_2O_{21}$ (R = Y, Er) and the complex rhombohedral phase based on ($R\overline{3}$) for $R_{10}Mo_2O_{21}$ (R = La, Nd). The bixbyite phase is metastable and is formed due to kinetic factors in the stability field of lower symmetry phases: pseudotetragonal (T) and rhombohedral ($R\overline{3}$).

The mechanical activation of $5Ln_2O_3 + MoO_3$ (Ln = Nd, Er) mixtures containing unmilled or premilled MoO_3 initiates the formation of $Ln_{10}Mo_2O_{21}$ (Ln = Nd, Er) at room temperature, which is accompanied by a reduction in the ESR signal from Mo^{5+} paramagnetic ions located on the surface of the activated MoO_3 and, hence, by a reduction in the amount of MoO_3 in the mixture, due to reaction with Ln_2O_3 (Ln = Nd, Er).

A different situation was observed when we have used mechanical activation of $5R_2O_3 + MoO_3$ (R = La, Y), where La, Y are non-magnetic cations. Although XRD shows a decrease of MoO_3 diffraction lines intensity in the process of mechanical activation with an increase of grinding time from 10 to 120 min, but this is accompanied not by decreasing, but increasing in the ESR signal from Mo^{5+} paramagnetic ions.

High-temperature annealing of mechanically activated precursors at 1500–1600 °C, 3 hours leads to the formation of the rhombohedral ($R\overline{3}$) phase for $Y_{10}Mo_2O_{21}$ and the complex rhombohedral phase for $La_{10}Mo_2O_{21}$ with parameters that are related to those for the following ratios: $C = C_R / \sqrt{3}$; $A = A_R \times 2 / \sqrt{14}$, [2].

The temperature dependence of the total (electronic and ionic) grain interior conductivity of one of the best electron-proton conductor $La_{10}Mo_2O_{21}$ in wet air was extracted from impedance spectra obtained using a P-5X potentiostat/galvanostat combined with frequency response analyzer module (Elins Ltd, Russia) over the frequency range of 500 kHz to 0.1 Hz at signal amplitude of 150 mV in the temperature range of 100–900ºC. A systematic increase of total conductivity in wet air as compared to the conductivity in dry air is indicative of hydration of the samples resulting in proton conductivity. The proton contribution in $La_{10}Mo_2O_{21}$ exists up to 900°C and is 5× 10^{-4} S/cm at 800°C and 5× 10^{-5} S/cm at 600°C.

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Experimental evaluation of diesel cogeneration system for power and drying of aromatic herbs

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Waste heat from diesel engine exhaust gases was recovered to heat air using a thermosyphon heat exchanger. The air heated was used in a convective tray dryer for drying Origanum, Mentha Spicata and Basilicum. Experiments were carried out at full load in a stationary compression ignition engine coupled with a generator. The maximum global energy efficiency of this cogeneration system was 40.14% and the effectiveness of the heat exchanger was 39%.

Effect of sodium and calcium on the ash fusion temperatures of Zhundong coal

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It is estimated that Zhundong coalfield has a tremendous reserve of 390 billion tons, which is regarded as the largest contact coalfield in China and even all over the world at present [1]. Zhundong coal can provide China with a secure energy supply in the impending decades in light of current coal consumption, thus playing an important role in China's future energy consumption. Zhundong coal is a typical lignite or sub-bituminous coal characterized by the features of high moisture, low ash and sulfur contents, which is a promising clean fossil fuel [2]. However, Zhundong coal has high alkali and alkali earth metal (AAEM) content [3, 4], especially rich in sodium and calcium. Unfortunately, several severe ash related issues such as fouling, slagging, and high temperature corrosion, are caused in boilers when Zhundong coal is applied in power plants [3, 5-7], despite sodium and calcium salts exhibit excellent catalysis for coal thermal conversion [8, 9]. Therefore, it is imperative to understand the ash fusion characteristics to mitigate ash related risk during Zhundong coal combustion. It is generally considered that coal ash fusibility is one of the important factors for insight into the slagging and fouling behaviors inside gasifiers and boilers in the industrial practice. AFTs are widely used to evaluate the ash fusibility because they can not only provide the detailed information about the ash softening and melting behavior but also present the indication about the progressive melting process from ash to slag [10-13]. In this study, The effect of sodium and calcium on the ash fusion temperatures (AFTs) of Zhundong coal was investigated in this study using an ash fusibility tester combined with X-ray diffraction (XRD) technology. The results indicate that the AFTs of Zhundong coal are closely related to the content of sodium and calcium in coal ash composition. The pretreatment of the raw coal with water leaching and hydrochloric acid leaching can remarkably enhance the AFTs, which is attributed to the removal of inherent alkali metal species in coal. The AFTs decrease first and then increase with the increment of Na_2CO_3 loading and the minimum AFTs was reached at 15 mass % Na_2CO_3 loading. The transformation of hematite during ashing of Zhundong coal with different Na_2CO_3 loading gives much contribution to the reduction of the AFTs. Meanwhile, the formation of KSi_3AlO_8 and muscovite accounts for the rising AFTs beyond the loading amount of 15 mass % Na_2CO_3. The effect of CaO addition on the AFTs of Zhundong coal resembles that of Na_2CO_3. The AFTs first gradually decrease and then strikingly increase with the increment of CaO content, and reached the minimum at 10 mass % CaO addition. The drop of AFTs maybe results from the formation of low-melting iron species and eutectic salts, whereas the growing AFTs may be ascribed to the formation of Ca_2SiO_4 during the ashing of Zhundong coal added CaO.

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Phase change materials based on recycleable thermosetting polymers for thermal energy storage

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Keywords: phase change materials, thermal energy storage, thermosetting polymers, recyclable

Phase change materials (PCMs) for renewable thermal energy storage are beneficial to solve energy crisis and environmental deterioration. Particularly, PCM based on polymers have drawn extensive attraction due to their superior properties. Thermosetting polymers can provide reliable restrict effect and robust mechanical properties, while thermoplastic polymers are capable of giving PCMs excellent recyclability and reprocessability. Here we report an economical feasible, facile, eco-friendly method with a dynamic crosslinks for thermosetting PCM to obtain both good thermal storage capacity and recyclability. Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical composition of SSPCMs. Xray diffraction (XRD) and Polarizing optical microscopy (POM) were adopted to compare the crystalline properties of PCMs. Differential scanning calorimetry (DSC) was conducted to investigate the phase change properties before and after reprocessing. Thermogravimetric analysis (TG) was carried out to reveal the thermal reliability.

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Energy and exergy efficiencies of sensible thermal energy storage for large chp plant in poland

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Keywords: District Heating System, Combined Heat and Power, Sensible Thermal Energy Storage, Energy, Exergy

The work contains simplified energy and exergy analyses of the hydraulic system with the Thermal Energy Storage (TES) circuit for one, selected Combined Heat and Power (CHP) plant, which supplies heat to the District Heating System (DHS). Energy and exergy efficiencies were estimated for the 'Blocks Part' of CHP plant Siekierki in Warsaw. This plant is the biggest CHP plant in Poland and the second biggest in Europe. Installed heating and electrical capacities are 2078 MW_{th} and 622 MW_e respectively. The CHP plant Siekierki has been in operation since 1961. The 'Blocks Part' consists of three Heating Blocks with nominal electrical capacity of 110 MW_e and heating capacity of 175 MW_{th} each.

A sensible, thermocline TES system consists of a tank, a storage medium and inlet/outlet devices. Energy in this TES system is stored by changing the temperature of the storage medium and the amount of energy is proportional to the difference between the storage inlet and outlet temperatures, the mass of the storage medium and its heat capacity.

Energy and exergy analyses were performed for the heating season (the highest outside temperature $T_e = -20$ °C, i.e., calculating conditions), intermediate season (average temperature $T_e = 1$ °C) and summer season (average temperature $T_e = 15$ °C). The presented results of the analyses allow one to determine the places of highest exergy destruction in the hydraulic system with the TES loop, and hence open up an opportunity to carry out appropriate mitigating action. Detailed results of the energy-exergy analysis show that both energy consumption and exergy destruction rate in respect of operation of the hydraulic system of CHP plant with TES, for charging and discharging cycles of the tank are relatively low, i.e., the power of the additional equipment (TES pumps) equates to 0.5–0.8% of the total power of the heating block and exergy destruction rate is at the level of a few hundred kW.

Exergy, Experimental thermodynamics

Simultaneous measurements of the pvt and thermal pressure coefficient of 2-propanol and derived values of internal pressure in the critical and supercritical regions

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Keywords: heat -transfer mechanism, heat capacity, laser-flash method, thermal conductivity, thermal diffusivity

The high-temperature, high-pressure, nearly constant-volume adiabatic piezo-calorimeter [1] was used for accurate simultaneously measurements of the PVT relationship and thermal pressure coefficient, $\gamma_V=(\partial P/\partial T)_V$, of 2-propanol in the critical and supercritical regions. The measurements were made along the 10 selected isochors (6 liquid and 4 vapour) between (265 and 643) kg·m^{-3} and over a temperature range from (346 to 616) K at pressure up to 9.17 MPa. The most measurements were focused in the immediate vicinity of the critical and phase transition temperatures in order to accurately determine the phase transition parameters (T_S, P_S, ρ_S) in the critical region. The standard uncertainty of the density, temperature, and isochoric heat-capacity measurements is estimated to be 0.1 %, 0.02 K, and 1.5 %, respectively. Measured values of phase transition parameters near the critical point (the top of the coexistence curve) were used to estimate the critical parameters of 2-propanol, $T_C = 508.72 \pm 0.5$ K and $\rho_C = 268.82 \pm 5$ kg · m^{-3}. The measured values of the PVT data and thermal pressure coefficient $\gamma_V = (\partial P/\partial T)_V$, were used to calculate internal pressure (or energy-volume coefficient) as $(\partial U/\partial V)_T = T(\partial P/\partial T)_V – P$ [2, 3]. Internal energy-volume coefficient $(\partial U/\partial V)_T$, is very sensitive to changes in the structure of the liquids and nature of the intermolecular interactions. In the same experiment we also measured calorimetric properties such as isochoric heat capacity which is defined as $C_V = (\partial U/\partial T)_V$. Therefore, the present technique allows to simultaneously measuring both temperature $C_V = (\partial U/\partial T)_V$, and specific volume derivatives, $P(\partial U/\partial V)_{T\mathrm{int}}$, of internal energy, U(T, V). The pressure and temperature effects on the internal pressure behaviour of 2-propanol have been studied. The derived values of internal pressure were used to study of the statistical structure factor S(Q) 2-propanol in the critical region as

$$S(Q) = \left[1 - 6\left\{1 - \frac{P_{\mathrm{int}}}{\rho k T}\right\}\left(\frac{X\sin x - x\cos x}{x^3}\right)\right]^{-1}$$

The singular behaviour (divergence) of the first temperature derivative of the internal pressure (dP_{int}/dT) at the critical point was observed. Locus of the zero internal pressure points for 2-propanol was studied.

Acknowledgments
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Numerical investigation of two single-phase force convection in circular micro-channel

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Keywords: Experiment validation, CFD, Heat transfer, microchannel

Now a days huge demand on many electronic devices such as laptop, cell phone and so on. The heat generated by The electronic component increases due to density increasing. Implementing microchannel could be a good solution to despite the head. Moreover, Microchannel could be use for many aspects that is required a high heat removal such as micro miniature refrigerators, microelectronics, micro heat pipe spreader, fuel processing biomedical and aerospace etc. therefor many researches have been done to microchannel. In this study an investigation has been done for the circular microchannel inside a 45 mm dimeter container. The fluid for the container is oil and keep stationary. The force convection is applied for water to passes through micro channel pipe. The number of micro channel is 79 with hydraulic dimeter as 279 µm. This study start with validation of lab work by varying the Renduls number and water inlet temperature, then a Computation fluid Dynamics model performed to investigate the two single-phase force convection in circular micro-channel.

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Discussion on the influence of coal dust dispersion pressure on minimum ignition temperature

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Keywords: minimum ignition temperature, dispersion pressure, coal dust, flame propagation

The minimum ignition temperature (MIT) of a dust cloud is a vital parameter with dust hazards. Its analytical approach follows BS EN 50281-2-1:1999, and it specifies the amount of sample and dispersion pressure during the test. Numerous studies have shown that sample mass has a prominent effect on the MIT, but there is scant literature on the influence of dispersion pressure. In this study, coal dust ,which stood in a 50 °C drying oven for 24 hours and confirmed the water content <2 mass%, was used in the MIT test to observe the influence of different dispersion pressures (0.05, 0.1, 0.2, 0.3, and 0.5 bar) on MIT. The lower dispersion pressure caused less coal dust to enter the apparatus. The most obvious was that only 24.3 mass% of coal dust entered the furnace with a dispersion pressure of 0.05 bar. In addition, the test results showed that the effect of dispersion pressure on MIT is not significant, and the difference of MIT was 5 °C when the dispersion pressure was 0.05 (MIT= 585 °C) and 0.5 bar (MIT= 580 °C). As far as the performance of flame propagation, a higher dispersion pressure was indeed significantly better than the lower dispersion pressure. According to the test results, the dispersion pressure had little effect on judging the MIT combustion temperature, but it had a great influence on the amount of dust entering and combustion phenomenon. Among them, when the dispersion pressure was <0.3 bar, the amount of sample entering the furnace and the state of combustion was poor. Therefore, the MIT test of coal dust recommended the dispersion pressure should be greater than 0.3 bar.

Acknowledgments

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A new fractional-order anomalous heat-conduction equation within the weakly singular kernel

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Keywords: heat-conduction equation, exact solution, fractional derivative, Laplace transform

In this talk, the new fractional-order heat-conduction equation is proposed for the first time. The fractional order derivative operator exists the weakly singular kernel of power-law type is considered [1]. With the aid of the Laplace transform, the exaction with the different orders are discussed in detail. The new factional derivative formula is accurate and efficient for the description of the anomalous heat-transfer problem.

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Fuels, biofuels

Metal-organic framework catalysts for efficient liquid biofuel production

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The objective of this research work is to develop a new class of catalysts made of earth abundant, low cost, chemically stable and non-toxic materials that can generate at globally significant rates, efficiencies and scales, biofuels such as butyl butyrate. The thrust of this research project is to understand at a fundamental level the relations between the synthesis, composition, structure and properties of champion materials that confer upon them the capacity to function as efficient esterification catalysts. For this purpose, Zr-based Metal-Organic Frameworks were synthesized and characterized using different techniques such as XRD, BET, SEM and TGA and their acid density was evaluated using back titration.

All prepared catalysts were successfully used for the catalysis of the esterification reaction of butyric acid in presence of butanol for the production of butyl butyrate. Catalysts with higher acid density lead to higher conversion rates, and higher catalyst loadings also increased the conversion to butyl butyrate. The UIO-66$(COOH)_2$ catalyst lead to 91% conversion, very close to the 96% conversion achieved by the conventional homogeneous liquid catalyst H_2SO_4. All catalyst were easily separated from the reaction medium, recycled, and efficiently reused as catalysts for new esterification reactions without significant loss in activity. With this knowledge, catalytic conversion rates and efficiencies of materials can be engineered from a laboratory prototype and optimized to a technologically important archetype able to make biodiesels at a globally significant scale.

Investigations on pyrolytic and gasification behavior of textile industry sludge

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Keywords: textile industry sludge, pyrolysis, gasification, TGA-FTIR, kinetics, thermodynamics

Industrial and commercial development of India have tremendously enhanced the waste generation in last few decades. One of the most critical issues with treatment and disposal of waste concerns management of huge quantities of sludge generated from effluent treatment plants (ETPs) installed textile, paper, food and textile [1]. Textile dyeing industry is one such industry in which the sludge generated in ETPs consist of dyes, persistent biodegradation products such as polycyclic aromatic hydrocarbons and heavy metals. The traditional disposal of textile industry sludge (TIS) in soil and/or landfills is neither an environmentally suitable option nor it is socially acceptable. Co-combustion of TIS is one of the alternative way of disposing owing to development in combustion technology. This option minimizes the waste volume, reduce the fuel costs and leads to ash stabilization as well [2]. In the present work, co-combustion and pyrolytic behavior of TIS under O_2/N_2 and O_2/CO_2 atmosphere have been evaluated by applying a thermogravimetric analysis (TGA) methodology coupled with FTIR. Raw TIS sludge has been characterized by various techniques such as XRD, EDX, XRF, CHNS analysis, FTIR, etc. Degradation kinetics has been evaluated by various kinetic models. Degradation kinetics of combustion and pyrolysis of TIS has been evaluated using iso-conversional Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) models. The kinetic parameters calculated have been used to calculate the changes in thermodynamic parameters, the enthalpy (ΔH), Gibbs free energy (ΔG) and the entropy (ΔS).

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Artificial neural networks to assess thermal stresses in cylinder head of a spark ignition engine fueled with ethanol-gasoline blend

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Keywords: cylinder Head; ethanol-gasoline blend; neural networks; temperatures;thermal Stress

This paper is investigated thermal stresses analysis in cylinder head of a spark ignition engine fueled with ethanol-gasoline using neural network predictors. The investigation is divided into two stages. First stage; the thermal stresses in the cylinder head of an internal combustion engine are determined as a function of the level of temperature. Measuring the temperatures in different parts of the cylinder head, the cooling can be adjusted or the materials can be improved, or even the properties of the fuels can be improved. The second step of the study; according to experimental results, some neural network predictors are used modeling thermal stresses in cylinder head a spark ignition engine. Three types of ANNs are used to compare each other. From the results, it is noted that the proposed Radial Basis Neural Network gives the best results for analyzing thermal stresses.

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Geosciences and minerals

Thermal behaviour of Estonian phosphorites from different deposits

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Keywords: IR-spectroscopy, phosphorites, thermal analysis, XRD

Thermal behaviour of three Estonian phosphorite ores from different deposits (Iru, Toolse, Ülgase) and their concentrates obtained by cationic enrichment of ores have been studied. Estonian phosphorites are fluorcarbonate apatite (francolite) type of phosphorites, while among admixtures quartz, dolomite, calcite, pyrite, bassanite, hematite and organic matter prevail.

The experiments on a Setaram Labsys Evo 1600 thermoanalyzer coupled with Pfeiffer Omnistar Mass Spectrometer were carried out under non-isothermal condition at the heating rate of 10°C min^{-1} up to 1200°C in an oxidizing and inert atmosphere containing 79% of Ar and 21% of O_2 or 100% Ar, respectively. Standard 100 µL alumina crucibles were used, the mass of samples was 15±0.5 mg. For XRD and FTIR analysis the samples were heated up to 500, 950 or 1200°C with the heating rate of 10°C per min with following storing of them at these temperatures by 30 min and afterwards quick cooling down to room temperature. The XRD analysis was performed with a Bruker D8 Advance Diffractometer and FTIR analysis with Bruker ALPHA. The influence of thermal treatment of samples on the solubility in 2% citric acid was also studied.

The emission of hygroscopic water and, in addition, crystal water from dehydration of bassanite from Ülgase phosphorite prolonged up to 200–220°C. The emission of carbon dioxide and water, resulting from thermooxidation of organic matter took place in the temperature interval from 200 up to 500–550°C. Thermooxydation of pyrite contained in Iru and Ülgase samples with emission of SO_2 into the gaseous phase started at around 380°C and prolonged up to 520°C. At these temperatures part of formed sulphur dioxide was bound by carbonates and fluorcarbonate apatite into the solid phase with formation of $MgSO_4$ and secondary $CaSO_4$. Thermooxidation of organic matter and pyrite took place even in neutral gaseous atmosphere due to the oxygen containing in organic matter, but less intensively comparing with those occurring in oxidizing atmosphere.

At temperatures from 600–650°C up to 1100–1150°C the mass loss with the emission of CO_2 was partially caused by decomposition of carbonates (dolomite, calcite) with formation calcium and magnesium oxides, but mainly by emission of CO_2 from the structure of francolite. The emission of SO_2 at temperatures higher than 700–800°C was caused, especially in the neutral atmosphere, by decomposition of $MgSO_4$ formed at lower temperatures, and at temperatures higher than 1100°C by starting the decomposition of secondary $CaSO_4$ and from structure of sulphated francolite. The total mass loss of samples heated up to 1200°C was, depending on the phosphorite deposit, between 4.3 and 7.9%.

The results obtained indicate the complicated character of transformations occurring at thermal treatment of Estonian phosphorites and certain differences depending on the composition of samples and gaseous environment.

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Thermal properties of ethylene-vinyl acetate copolymer with coal ash and layered double hydroxide composite as flame retardants

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Keywords: Ethylene-vinyl Acetate, Layered Double Hydroxide, Flame resistance, Retardant, Limiting oxygen index

The flame retardancy has always been a big challenge in the fire prevention of materials containing ethylene-vinyl acetate polymer (EVA). In case of fires, in appropriately flame-retarded EVA can even exacerbate the hazard, such as accelerating the combustion, releasing more heat, liberating substantial toxic gases and so forth. Nonflammable coal ash and Zn-Mg-Al contained Layered Double Hydroxide (LDH) were used to synthesize Coal-LDH Composite (CLC) were prepared by using the in-situ co-precipitation method aiming to retard the combustion of EVA. The results show that the crystalline degree of CLCs decreases with increasing the mass fraction of SFC. The morphology of Zn/Mg/Al-LDHs on the surface of CLCs can be controlled through changing the oxidation temperature of SFC and the crystallization time. Then, CLC/EVA composites with different CLC contents were made for tests including mechanical properties, surface configuration properties and releases of heat and smoke. Studies conclude that CLC additions of less than 15% can enhance the tensile strength of EVA due to the massive nano-fibers existing on CLC/EVA interfaces. Experimental tests also indicated that the addition of CLC can effectively increase the Limiting Oxygen Index (LOI) of EVA. A CLC addition of 13.7% could change the EVA from inflammable to nonflammable material. With the increase of CLC addition, the times to ignition and to maximum heat release rate were both prolonged and the fire growth index was decreased at the same time. Additionally, the addition of CLC could effectively reduce the combustion process of EVA because carbon layers could be formed on the surface of the samples and therefore blocked the oxygen penetration to the inside of EVA.

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Adsorption mechanism study of xanthates on pbs by titration microcalorimetry

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Keywords: microcalorimetry, xanthates, flotation, adsorption, lead sulphide, galena, Raman spectroscopy

Isoperibol (pseudo-adiabatic) titration microcalorimetry was used to study the adsorption mechanisms of xanthates [CH3(CH2)nOCS2-] at the PbS/aqueous solution interface. The effect of the xanthate alkyl chain length (2n to 4n) on the adsorption heat was evaluated. Xanthate adsorption isotherms were also determined. Furthermore, the amount of SO4 into the aqueous solution as xanthate uptake proceeded was quantified. The adsorption isotherms and the adsorption heat of the xanthates showed two steps. The first step occurred within a monolayer xanthate coverage that was attributed to chemisorption of the xanthate polar group with surface OH to form CH3(CH2)nOCS2Pb. Lead xanthate (CH3(CH2)nOCS2)2Pb multilayers formed in the second step that was attributed to an ionic exchange chemical reaction between the xanthate and PbSO4, wherein this PbSO4 resulted due to surface oxidation of the PbS. In the chemisorption step, the heat was found to be independent of the xanthate alkyl chain length and to linearly decrease in magnitude as the xanthate adsorption increased. In the xanthate multilayer step, the magnitude of the integral heat increased with the chain length of the xanthate. Heat contributions due to both the alkyl chain length and the interaction between the xanthate polar group and PbSO4 for the formation of lead xanthates are presented. Raman spectroscopy was used to characterize the lead xanthate multilayers on PbS.

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Adsorption mechanism study of xanthates on Pbs by titration microcalorimetry

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Keywords: microcalorimetry, xanthates, flotation, adsorption, lead sulphide, galena, Raman spectroscopy

Isoperibol (pseudo-adiabatic) titration microcalorimetry was used to study the adsorption mechanisms of xanthates [CH3(CH2)nOCS2-] at the PbS/aqueous solution interface. The effect of the xanthate alkyl chain length (2n to 4n) on the adsorption heat was evaluated. Xanthate adsorption isotherms were also determined. Furthermore, the amount of SO4 into the aqueous solution as xanthate uptake proceeded was quantified. The adsorption isotherms and the adsorption heat of the xanthates showed two steps. The first step occurred within a monolayer xanthate coverage that was attributed to chemisorption of the xanthate polar group with surface OH to form CH3(CH2)nOCS2Pb. Lead xanthate (CH3(CH2)nOCS2)2Pb multilayers formed in the second step that was attributed to an ionic exchange chemical reaction between the xanthate and PbSO4, wherein this PbSO4 resulted due to surface oxidation of the PbS. In the chemisorption step, the heat was found to be independent of the xanthate alkyl chain length and to linearly decrease in magnitude as the xanthate adsorption increased. In the xanthate multilayer step, the magnitude of the integral heat increased with the chain length of the xanthate. Heat contributions due to both the alkyl chain length and the interaction between the xanthate polar group and PbSO4 for the formation of lead xanthates are presented. Raman spectroscopy was used to characterize the lead xanthate multilayers on PbS.

Acknowledgments

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Relating enthalpy of immersion to mineral flotation performance

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Keywords: Enthalpy of immersion, wettability, mineral flotation

The enthalpy of immersion is the heat change arising from the replacement of the solid-gas interface with the solid-liquid interface when a solid surface is immersed in a liquid. Although immersion calorimetry has been established as a reliable means of determining wettability of solid surfaces, it has found only limited applications in flotation research where wettability of mineral ores is a key variable. In this study, precision solution calorimetry was employed to measure the enthalpies of immersion of different minerals in water. These values were then related to the recoveries and first-order flotation rate constants as determined by microflotation. The same measurements were also made of sulphide minerals whose surfaces were modified using different percentage coverages of a hydrophobising surfactant.

It was found that there was a strong inverse relationship between the enthalpy of immersion of the minerals studied and their wettability as indicated by their recoveries and rates of flotation in a microflotation cell. In addition, a critical enthalpy of immersion (CEI) value was observed above which no flotation occurred. The variance in the inverse relationship between enthalpy of immersion and rate of flotation decreased when the data was normalized with respect to particle density which was the only variable in the flotation studies with respect to particle-bubble encounter efficiency. These results have shown that the enthalpy of immersion is an excellent indicator of both the natural mineral hydrophobicity and of the extent to which collectors render a mineral hydrophobic. This technique has considerable potential to be used as a highly sensitive measure of mineral surface wettability in predicting flotation performance.

Dehydroxylation entalphy standards to the quantification of al-goethites

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Keywords: Goethite, DSC, Mineralogical quantification

The primary objective of this study is to establish a procedure for the synthesis and characterization of a set of Al-goethites with different amounts of Al-for-Fe substitution (range from 9 to 28%) to be used as heat-of-reaction (dehydroxylation) standards in the quantification of goethite by Differential Scanning Calorimetry (DSC). The procedure could be used as a supporting method in the comparison and validation of older and newer methods for the mineralogical quantification in valuable geological material (e.g., soils, laterites, bauxites). The increasing order of Al-for-Fe substitution in planned syntheses was confirmed by XRD, XRF, DSC and SEM results, which showed that a small database of goethite dehydroxylation standard enthalpies could be established in this study. Two primary endothermic peaks are always expected and were detected in all samples: the first endothermic peak at 60–150ºC was caused by the release of adsorbed water, the amount of which depends on the particle size and the pretreatment of the sample; and the second endothermic peak at 200–350 ºC was caused by dehydroxylation. In the case of Al-goethites, a double dehydroxylation endotherm is expected [1,2-5]. However, the dehydroxylation region of the synthetic goethitic products is consistent with that of complex materials, indicating a mixture of goethites with different percentages of Al substitution, which is typical of metastable phases, even though the extreme products of the solid solution goethite are stable (0 and 33% mol Al) [1]. The production of standards of multiple goethite varieties is so important than one goethite standard alone, because such mixtures are thermodynamically common in nature, and therefore, very common in rocks.

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Heat transfer

A study on the control of thermal performance using bimetal fin channel in heat exchagner

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Keywords: bimetal fin, calorific value control, phase change material, latent heat storage, heat exchanger

Thermal energy storage is a key technology essential to effective use of intermittent energy sources, such as solar thermal energy. Among various thermal energy storages, latent heat thermal energy storage (LHTES) is being actively studied because of its high heat storage capacity [1]. It has approximately five to 14 times higher heat storage capacity than convectional thermal energy storage technology [2].

The LHTES for domestic hot water application involves two processes: charging and discharging. Thermal energy is stored in and extracted out of the PCMs through charging and discharging. However, the slow charging/discharging rates and the unreliable LHTES discharging temperatures caused by the low thermal conductivity of the PCM are two obstacles in the practical application of the LHTES [3]. Nowadays, much research is being conducted to develop various types of LHTES using PCMs to address the slow charging/discharging problem.

In this study, we proposed the bimetal fin channel for the temperature-dependent flow rate controlling device to address the problems related to the slow and unreliable charge/discharge time and water temperature of the LHTES, respectively. A bimetal fin is a new type of metallic fin in which two metals with different thermal expansion coefficients are attached to each other. The bimetal fin changes its form by bending according to the water temperature.

This paper reports on the development of a new type of heat exchanger with bimetal fins for controlling the calorific value of water through phase change material (PCM) heat storage. It presents detailed numerical and experimental data on the velocity and temperature of water flow in a channel equipped with bimetal fins on the wall. Computational fluid dynamics and particle image velocimetry are used to analyze the flow behavior around the bimetal fins. The bimetal fins increase the insulation performance at the wall, such that the heat loss rate is decreases by a maximum of 56%. Furthermore, the flow rate and calorific value can be controlled at 10 L/min and 50 kJ, respectively. Consequently, the discharging-time during which hot water can be generated increases by a maximum of 70 min.

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Reactivity of fluororubber modified aluminum in terms of heat transfer effect

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Keywords: fluororubber, aluminum, heat transfer, modeling

Reaction performance of aluminum after explosion plays an important role in the whole energy release level of aluminized explosives. Under explosive atmosphere heat transfer efficiency of the aluminum particle will be a key factor that determines when the reaction of aluminum starts [1]. As it is known to all, alumina has a high melting point and can hardly be removed by melting off which greatly impedes aluminum reacting with explosive products. In this work, we proposed a premium core-shell heat transfer structure to benefit the reaction performance of aluminum. In this structure, fluororubber served as the shell which coated aluminum inside. Fluororubber was chosen to be the shell not only because of its superior heat conductivity in need but also of its high heat release when reacted with aluminum. The heat transfer model after explosion constructed based on the core-shell sphere theory and due to the superfast process was therefore simplified with following assumptions:

1. Specific heat capacities and heat conductivity coefficients of both materials kept constant;
2. Heat loss caused by radiation from aluminum to surrounding was ignored;
3. Relative motion between aluminum and gas products didn't take into consideration.

The heat transfer model was therefore as following:

$$\frac{\partial T}{\partial t} = \alpha_i \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad i = 1, 2 \qquad (1)$$

In the model, αi is the thermal diffusivity [m2·s-1], αi=ki/(ρiCi), ki is the heat conductivity [W·m-1·K-1], ρi is the density [kg·m-3], Ci is the specific capacity[J·kg-1·K-1], i=1 represent the core material, i=2 represent the shell material.

The heat transfer difference was shown in Fig 1, there was huge temperature difference between core and shell for modified aluminum, which benefited the temperature increasement in the surface and therefore sped up the decomposition of fluororubber. While for traditional aluminum with Al2O3 as the shell, temperature slowly rose and there was slight difference between core and shell. Through systematic calculation, the fluororubber could completely decompose within ten nanoseconds with diameter of no more than 200 nm. This strongly put forward the reaction of aluminum with explosion products and therefore elevated the whole energy release. Under the same condition, the aluminum with oxide shell would much delay the reaction. Detonation velocity tests further confirmed the calculations. Explosive with fluororubber modified aluminum could reach a velocity of 11% higher than that of its counterpart. The enhancement in the velocity clearly showed that the fluororubber modified aluminum participating in the detonation process.

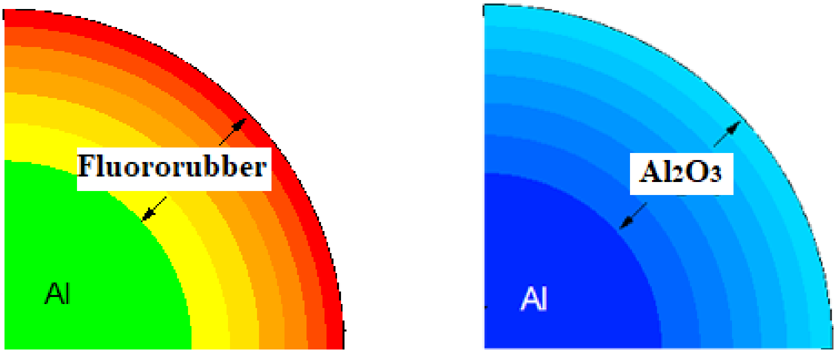

Fig 1. Different behaviours in heat transfer between modified aluminum and traditional aluminum

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Inorganic materials

Complexation abilities of multifunctional N,O-donor ligands toward d-block metal ions – structural and thermal aspects

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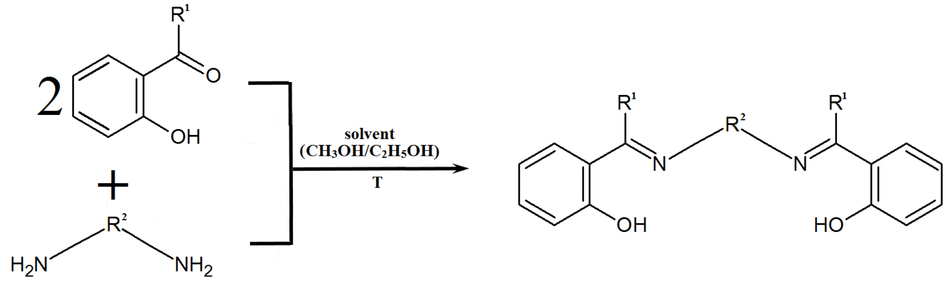
Keywords: Schiff base, metal complexes, thermal analysis, crystal structure

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals[1-4]. This provides the opportunity to design new systems selective for specific metallic ions. Nowadays the research field dealing with Schiff bases coordination chemistry has expanded enormously due to their interesting properties and potential applications in various areas such as catalysis, luminescent probes, analytical chemistry, magneto-structural chemistry, agrochemical, biological fields etc. Among this type of ligands special attention is paid to the Schiff bases formed during the reaction of diamines with *o*-hydroxy aldehydes and ketones [1, 3-5]. The structure of these type of imine compounds is stabilized by the intramolecular, strong hydrogen bonds (O-H···N) which forming the six membered ring where the proton transfer from the phenolic oxygen to the imino nitrogen atom is often observed. As a result, the compounds can exist in the phenol-imine (OH), keto-amine (NH) or zwitterionic ($N^+{-}H\cdots O^-$) forms exhibiting interesting properties like solvato-, thermo- and photochromism [4, 5].



where R^1 = aryl derivatives (CH_3-; C_6H_5-) R^2 = $CH_2CH(OH)CH_2$

Scheme 1 Synthetic pathway for the preparation of the azomethine ligands

The aim of our study was the synthesis of N,O-donor Schiff bases using 1,3-diamino-2-propanol and *o*-phenolic ketones (Scheme 1) and determined of their complexation ability towards chosen metal ions. The subject of studies was also investigation of influence of synthesis conditions (such as type of solvent, temperature and stoichiometric ratio M:L) on the final product of the metal ion complexing process as well as their structure and thermal properties. The studied Schiff bases contain in their structure N2O3-donor atoms which allowed to obtain mononuclear or polynuclear metal complexes depending on the synthesis conditions. The compounds are stable at room temperature. Thermal behaviour of complex was studied by means of TG-DSC (in air atmosphere) and TG-FTIR (in nitrogen atmosphere) analyses. The thermal decomposition of solvates is preceded by the desolvation process. Then, in the case of polynuclear complexes the acetate ions are removed from the structures which were confirmed by the FTIR spectra of gaseous products. The thermal degradation of the Schiff bases occurs in consecutive reactions where at first ammonia and HNCO/CH_3NCO bands appears in FTIR spectra confirming that azomethine double bonds firstly undergo the destruction.

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Analysis of DTA and dilatometric data used to study the behaviour of a mould flux

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Keywords: mould fluxes, crystallization, dilatometry, differential thermal analysis

Mould fluxes, known also as casting powders or mould powders, are used in steel continuous casting in order to control both (i) the heat extraction rate, during the solidification of the steel, and (ii) the lubrication of solidifying steel shell against the mould wall. Suitable heat extraction and adequate lubrication guarantee the stability of this process. These powders are synthetic slags formed by a complex mix of oxides and minerals. The main oxides present are SiO_2, CaO, and Na_2O, with a binary basicity (CaO/SiO_2 ratio) between 0.7–1.3. They also contain fluorite (CaF_2) and carbonaceous materials (coke, graphite, etc.) in their compositions. During process, formation of crystals in the zone of the gap between the steel solidified shell and refrigerated copper mould (at temperatures between 600-900°C) plays a fundamental role because increase the thermal resistance changing the heat extraction rate from the steel to the mould [1].

In the present work a casting powder containing ≈ 36 wt% SiO_2, ≈ 31 wt% CaO, 13 wt% Na_2O, and 10 wt% CaF_2, was used as starting material. A mass of 10 g of the mould powder was placed in a graphite crucible and melted at 1300°C. After 15 minutes at this temperature, the melt was poured onto a stainless steel inclined plate. By this method, solid glass layers were produced, which were sectioned into bars 10–15 mm in length to be used in dilatometric tests. Some of these bars were ground to powder to perform DTA runs. Both tests (DTA and dilatometry) were carried out at different heating rates: 5, 10 and 15 ºC/min, in air atmosphere, up to 900°C. Data of glass transition temperature (Tg), and crystallization peak temperature (Tc) were obtained from DTA and dilatometric runs. From these data, several non-isothermal methods based on Kissinger [2], Augis-Bennet [3], Ozawa [4], and Cheng [5] models, were used to study the crystallization kinetics. Based on these models, the activation energy of crystallization (E), the frequency factor (ν) and the crystallization rate constant (k) were calculated. A subsequent study was followed to determine the Avrami exponent and the crystallized fraction. The crystallographic phases were determined by XRD and the microstructure of samples, treated between 400–900ºC, was observed by optical and electronic microscopy.

Both methods (DTA and dilatometry) showed a Tg about 480°C and two crystallization peaks, the first appears around 600°C (Tc1) while a second peak occurs around 700°C (Tc2). A good correlation of both E and ν values, determined by DTA and dilatometry, was obtained. According to the average of non-isothermal models, the peak Tc1 has associated to crystallization energy of 290 kJ/mol (DTA) or 330 kJ/mol (dilatometry) and a frequency factor ≈ 10^{16} s^{-1} (DTA) or ≈ 10^{19} s^{-1} (dilatometry). The second peak Tc2 presented smaller Ec (≈ 190 kJ/mol from DTA or ≈ 230 kJ/mol from dilatometry) and smaller ν (≈ 10^{9} s^{-1} from DTA or ≈ 10^{11} s^{-1} from dilatometry) than the peak Tc1. Thus, a lower crystallization rate for the peak Tc2 was obtained. From the degree of crystallization at different heating rates, the kinetics of formation of crystals was analyzed. The influence of these results on the heat extraction during the continuous casting process of steel is discussed. Finally, from the width of the glass transition region, determined by DTA and dilatometric curves, a model proposed by Moynihan [6] to estimate mould flux viscosity was successfully used.

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Heteronuclear CuII/ZnII-LnIII complexes with N,O-donor ligands – Synthesis, crystal structures and thermal properties

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Keywords: heteronuclear complexes, TG-DSC, thermal investigations, Schiff base, N,O-donor ligands, lanthanides

Schiff bases as heterodonor ligands are characterized by the possibility of selective as well as simultaneous coordination of various d-block metal ions with a smaller ionic radius (0.75-0.6 Å) e.g. Cu(II), Zn, Ni(II) ion, and also with a larger ion radius (1.06-0.85 Å), e.g. f-electron one which results in the formation of heteronuclear 3d-4f complexes (Fig, 1). The introduction of hydroxyl, carboxyl and amino groups during designing ligands increase the number of donor atoms and result in formation structurally diverse complexes interesting in terms of typology. The complexes of metal ions with N,O-donor ligands belong to chemically stable compounds, which allow not only to carry out the suitable analyses, but also causes steadily increasing their popularity due to the search of new, multifunctional materials characterized by the existence of the so-called magnetic memory. In the synthesised by us compounds based on Cu(II)/Zn and lanthanides(III) the paramagnetic centres are connected by double oxygen bridges derived from the deprotonated Schiff base. The N,O-donor ligand coordinated lanthanide(III) ions only through donor atoms of oxygen from methoxy/ hydroxyl groups or only through hydroxyl groups, respectively, located on the aromatic ring. In contrary the imino nitrogen atoms and oxygen atoms of the deprotonated hydroxyl groups of the Schiff base ligand are coordinated with cooper(II) or zinc ions. The thermal analysis of 3d-4f compounds allowed us to evaluate the presence of crystallization and/or coordination solvent molecules in the complexes and to determine the endothermic and/or exothermic effects connected with processes such as: dehydration, melting, crystallization and decomposition.

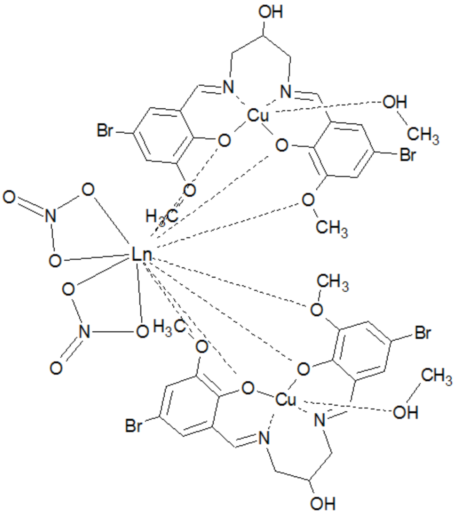

Fig. 1. Scheme of the Cu^{II}-Ln^{III}-Cu^{II} complex

Synthesis, characterization and thermal decomposition of hexaamminecobalt(III) permanganate – [Co(nh3)6](MnO4)3 – a precursor to prepare cobalt-manganese oxides.

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Keywords: cobalt complexes, permanganates, crystal structure, coordination compounds

The chemistry of hexaamminocobalt(III) salts is an intensively studied area, however, due to reducing character of the complex cation, the compounds formed with oxidizing anions, like permanganate are not very stable and hardly studied. The hexaamminecobalt(III) permanganate easily decomposes even under storage; thus only a piece of minimal information is available about its properties, and its thermal decomposition products have not been characterized at all. Since its decomposition temperature is lower than the typical decomposition temperatures of the cationic or anionic parts, a quasi-intramolecular redox reaction might take place at low temperature, in the solid phase, which gives a possibility to prepare cobalt-manganese oxides in amorphous and nanosize form. Similar reactions of tetraamminemetal (M=Cu, Zn and Cd) complexes gave nanosize MMn_2O_4 type spinels. The 1:3 Co:Mn stoichiometry and the valency range of Co and Mn (both elements have +2 and +3 oxidation state, and manganese might be stable in +4 oxidation state as well), during the Mn(VII)-Mn(II) redox reactions with the reducing NH_3 ligands coordinated in the compound, gives a challenge to identify the distribution of each type of cations in a given valence in these mixed oxides, e.g. between the tetrahedral and octahedral sites of spinels and likes. We studied the possibilities on the preparation of $(Co,Mn)Mn_2O_{4+x}$ or other catalytically active nanosize Co-Mn oxides from hexaamminecobalt(III) permanganate, together with synthesis and characterization of the precursor complex with powder XRD and vibrational spectroscopic methods, and TG and evolved gas analysis techniques. The products of the heat-treatment were characterized with IR, Raman, XRD, XPS, SEM and HRTEM methods.

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Polymorphism of Bi2O3-based compounds in Bi2O3-Ln2O3-WO3 (Ln = La, Pr, Nd) systems

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Keywords: Bi2O3, phase diagram, polymorphism, oxygen conductivity, DSC

Bi2O3-based solid solutions are interesting as promising oxygen conductors with conductivity reaching 0.1-1 S/cm at 800 °C. The pure Bi2O3 has a complex polymorphism. Four basic Bi2O3 phases are well known [1]: 1) α-Bi2O3 monoclinic phase, stable at room temperature; 2) β-Bi2O3 tetragonal phase; 3) γ-Bi2O3 cubic phase; 4) high-temperature δ-Bi2O3 cubic phase with fluorite structure, which is stable in narrow temperature range 700-780 ºC and demonstrate extremely high oxygen conductivity near 3 S/cm [2]. The main attention in literature is paid to δ-Bi2O3 phase stabilization, but complex polymorphism of Bi2O3-based compounds is also very interesting. Earlier, the ternary systems Bi2O3-Dy(Er)2O3-WO3 and Bi14W1-xLaxO24-3x/2 solid solutions were investigated with point of view of the stabilization of the oxygen-conducting δ-Bi2O3 cubic phase [3-5]. Similar Nd2MoO6-Bi2O3 and Bi2O3-Ln2O3-MoO3 (La, Pr) systems were investigated in our studies, where extensive stability fields of tetragonal and cubic compounds were found [6–8]. Full Bi2O3-Ln2O3-WO3 (Ln = La, Pr, Nd) systems with tungsten and large rare-earth cations have not been investigated.

This work is devoted to the study of phase formation and polymorphism of Bi2O3-based compounds in the ternary Bi2O3-Ln2O3-WO3 systems (Ln = La, Pr, Nd) using differential scanning calorimetry and electrophysical measurements.

Polycrystalline samples were obtained by solid state synthesis in the air. Low cooling rate (5 K/min) have been used to avoid metastable phases. Numerous phases with a cubic (δ and δ'), tetragonal (β and Bi14WO24-type), monoclinic (Bi3.24Ln2W0.76O10.14-type), and rhombohedral structure were observed in Bi2O3-Ln2O3-WO3 systems depending on Ln type and Bi2O3 concentration. The monoclinic Bi3.24Ln2W0.76O10.14-type compounds have the widest area of stability for all Ln (La, Pr, Nd). The high-temperature oxygen-conducting δ-Bi2O3 phase with a cubic fluorite structure stabilizes in all investigated systems in a narrow range of concentrations (85-90 mol.% Bi2O3). However, in the case of Ln = Nd, the additional stability field of cubic fluorite-type compounds (δ1-Bi2O3 phase) was found near the Nd2WO6-NdBiO3 join.

DSC investigations show, that cubic samples (δ and δ' phases) do not suffer phase transformation. Tetragonal samples with β-Bi2O3 structure and monoclinic Bi3.24Ln2W0.76O10.14-type compounds demonstrate complex polymorphism with two phase transitions at heating, and one transition during cooling. Above the phase transitions these compounds are transformed into high temperature cubic fluorite-type phase. One phase transition between tetragonal and cubic phases was found for Bi14WO24-type samples both for heating and cooling.

Cubic δ-Bi2O3 and tetragonal β-Bi2O3 samples demonstrate high electrical conductivity (~ 0.1-0.6 S/cm at 800 °C). The conductivity of monoclinic and cubic compounds with lower Bi2O3 concentration reaches 0.1-0.01 S/cm at 800 °C.

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Kinetics and catalysis

Applicability of incremental isoconversional methods to determine of the dependence of activation energy on the conversion degree corresponding to heterogeneous processes performed under arbitrary temperature programs

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Keywords: incremental isoconversional methods; arbitrary temperature programs; activation energy

The following incremental isoconversional methods can be used to evaluate the dependence of activation energy on the conversion degree of heterogeneous processes occurring in arbitrary temperature programs, including programs with constant heating rates: advanced non-linear isoconversional method (A-NL) [1]; integral incremental isoconversional method (Incr-int) [2]; differential incremental isoconversional method [3]; iterative incremental isoconversional method [4].

A-NL, Incr-int and Incr-dif methods are applicable only if for small intervals of the conversion degree, the dependencies temperature (T) vs. time (t) can be approximated satisfactorily with straight lines. For example, this condition is respected when using constant heating rate programs. However, it also uses temperature programs in which this condition is not desirable, e.g. sinusoidal modulated programs. For such programs, the correct values of activation energy are obtained by the IT method in which the temperature integral is performed numerically. Also, the A-NL method could be applied in these cases if the temperature integral to a determination would be evaluated as the sum of the integers corresponding to each linear portion of the T vs. t curve own to the range of conversion. Applying the procedure involves the initial drawing of the T vs. t for delimiting linear domains. Verification of this procedure was performed for simulated sinusoidal modulated data and experimental data obtained by TG analysis of HDPE under quasi-isothermal conditions. The values of the activation energy thus obtained are compared with those obtained by applying the Incr-int, Incr-dif and IT methods.

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How to use properly the distributed activation energy model?

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Keywords: Nonisothermal kinetics, distributed activation energy model, kinetic triplets, nonuniqueness, model-fitting

Distributed activation energy model (DAEM), originally proposed by Vand, assumes that a series of irreversible first-order reactions with different kinetic parameters that occurs simultaneously, which make it has a potential to approximate any complex reaction process. By overviewing its research history, most of works focus on how to simplify its complex mathematic expression, especially before 2000 in which the computer technology was not popular. Typically, Miura et.al [1, 2] proposed the two simple methods of DAEM model, which refer to Miura differential method and Miura–Maki integral method. Miura–Maki integral method has been utilized widely in many researches due to its easy-to-use. Yet many mathematic approximations in this simplified model may sacrifice its prediction ability. With the development of computer aided technology, some researchers began to use numerical method to solve DAEM, which is also called distribution-fitting method. Cai et.al [3] has done a large amout of works related to distribution-fitting method, and pointed out its disadvantage that different sets of kinetic parameters provide an acceptable fit accuracy at a single heating rate owing to kinetic compensation effect. In addition to that, different types of activation distribution function were also input into DAEM. Moreover, multi-components DAEMs were applied to fit multi-peaks mass loss curves. Compared to the simplified methods, the distribution-fitting method is able to ensure the prediction ability of DAEM, but nonuniqueness of kinetic parameter need to be solved. Some solutions for this problem are that one of kinetic parameters (activation energy or pre-exponential factor) or certain pre-exponential factor ($A=A_0T^m$, $A=e^{a+bE}$) are pre-set. Actually, this problem is still not solved due to human-made pre-set process. Unfortunately, the same problem is still appearing in many publications. In this work, the first aim is to appeal that the related researcher will not misuse the DEAM. Moreover, a feasible application solution of DAEM will be given. It is expected that this work may promote the healthy development of DEAM. The feasible solution is that **Step 1**: the values of activation energy at different conversion extents should be estimated based on the distributed activation energy model with distributed-free method; **Step 2**: the mean activation energy is obtained using the Maximum Likelihood Estimation based upon the values of activation energy at different conversion extents. **Step 3**: the estimated value of the mean activation energy is substituted into the activation energy distributed function, and the values of the standard deviation and pre-exponential factor for different heating rates are determined by using the numerical method. And the average values of the standard deviation and pre-exponential factors at different heating rates are treated as effective values. This solution can not only ensure the strong predicting ability, but also be helpful to get a set of effective kinetics parameters. The work will promote the application of the distributed activation energy model in the complicated reaction kinetics.

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An intersection method for evaluating the activation temperature (T_{op}) of a chemical reaction

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Keywords: activation temperature, onset temperature, Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TG), isothermal method, intersection method

The real activation temperature (T_r) is the initial temperature that a chemical reaction can really occur. Moreover, the onset temperature, widely accepted and taken as the activation temperature in thermal analysis, is doubtful both on theoretical and practical way. In this study, the activation temperature was obtained by the value at the intersection point of the extrapolated lines of the onset temperatures (T_o) and the peak temperatures (T_p) under differential heating rates in the thermal analysis. Both exothermic and endothermic decomposition reactions of six different types of materials were studied, indicating that the activation temperatures (T_{op}) of these reactions are well matched with the temperatures (T_{iso}) studied via isothermal experiment, while the difference between the onset temperature and that of the isothermal experiment is 30~70°C in previously published papers. The intersection method proposed in this paper will provide a simple way for accurately evaluating the activation temperature of a reaction, which indicates the thermal stability of materials and is important in new material design, synthesis and safety.

Study of oxy-combustion of plane tree (Platanus orientalis) seeds in O2/Argon atmosphere including kinetic analysis by the fraser-suzuki deconvolution for overlapping complex reactions

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Keywords: Oxy-combustion, Plane tree seed biomass; Combustion characteristics determination; Kinetic analysis; Fraser-Suzuki deconvolution; Asymmetrical kinetic curves

The combustion reactivity of plane tree seeds (PTS) biomass feedstock was studied using the thermogravimetry (TG). The effects of atmosphere (O_2/Ar) and different oxygen concentrations (O_2:Ar = 20:80 % and O_2:Ar = 50:50%) on the combustion characteristics were investigated. The results indicate that oxygen concentration show effectiveness on combustion of PTS. When combustion atmosphere changes from O_2:Ar = 50:50% to O_2:Ar = 20:80% (reducing oxygen concentrations), the burnout temperature increases by 29.50 ^{o}C for tested biomass and combustion process becoming more challenging. The obtained results demonstrate the ease of ignition of investigated lignocellulosic material for O_2:Ar = 50:50% ratio compared with O_2:Ar = 20:80% ratio, and the actual trend is maintained under the condition when the heating rate increased. The reducing of oxygen concentration strongly influenced on the amount of final residue products, particularly at higher heating rates (beyond 10 oC min–1). At the same time, the kinetic analysis of combustion profiles of PTS reveals different complex dependencies of both, the apparent activation energy (E) and the pre-exponential factor (log$A$) with conversion (α), especially in devolatilization and combustion of volatiles reaction regions. The large variation in E_α attributed to multiple parallel reactions was addressed through application of deconvolution technique utilizing the Fraser-Suzuki function as well as nonlinear mechanistic modeling, which also involves determination of composition of studied biomass. It was shown that Fraser-Suzuki equation very successfully and accurately fits the kinetic rate curves of entire combustion process, assuming the best selected the nth-order reaction model.

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Kinetic analysis of the Thermally induced transformations of calcium hydroxide in different gaseous atmospheres

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Keywords: calcium hydroxide, thermal decomposition, solid–gas reaction, impact of water vapor, kinetics

The atmospheric gas that contributes to the thermally induced reaction in the solid–gas system as the product or reactant is one of the most relevant factors to control the kinetics and mechanisms of the reaction. Because of the heterogeneous feature of the reactions in the solid–gas system, change in the atmospheric conditions imposes the dramatical change in the physico-geometrical reaction mechanism and overall kinetics in a complex manner of the interactions of the component physico-chemical reaction steps.

Thermally induced transformations of $Ca(OH)_2$ are such examples. The thermal decomposition of $Ca(OH)_2$ in flowing dry N_2 gas proceeds via partially overlapping two reaction steps attributed to surface and interfacial reactions [1]. The kinetic feature is described by the cumulative kinetic equation [2].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \sum_{i=1}^{N} c_i A_i \exp\left(-\frac{E_{\mathrm{a},i}}{RT}\right) f_i(\alpha_i) \qquad (1)$$

where c_i is the contribution of the reaction step i.

On heating $Ca(OH)_2$ in flowing N_2–CO_2 mixed gas, mass-change curve exhibits a smooth mass gain, which is invariant irrespective of CO_2 concentration (Figure 1(a)). The reaction is interpreted as the consecutive process of the thermal decomposition of $Ca(OH)_2$ and subsequent carbonation of CaO to form $CaCO_3$. The overlapping mass-loss and mass-gain processes that do not appear on the experimentally resolved mass-change curve can be simulated by the kinetic deconvolution analysis based on eq. (1) [1].

The thermal decomposition of $Ca(OH)_2$ is a typical reversible process in solid–gas system. Therefore, the water vapor pressure $p(H_2O)$ in reaction atmosphere restrains the reaction rate, indicating systematic shift of the mass-loss curve recorded under nonisothermal conditions at a selected heating rate to higher temperatures with increasing $p(H_2O)$ (Figure 1(b)). The kinetics of the reaction over different $p(H_2O)$ is universally described by introducing an appropriate accommodation function in the fundamental kinetic equation.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E_\mathrm{a}}{RT}\right) f(\alpha) a\left(p(\mathrm{H_2O}), P_\mathrm{eq}(T)\right) \qquad (2)$$

The practical kinetic analyses for those complex reaction processes are demonstrated in this presentation.

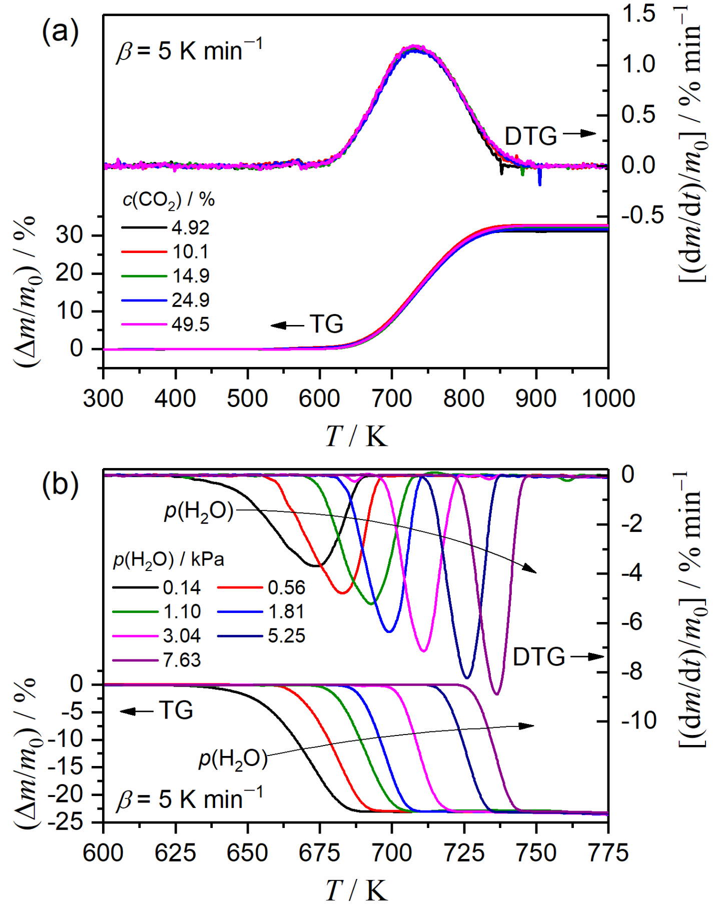

Figure 1. TG–DTG curves for $Ca(OH)_2$ recorded under different atmospheric conditions in flowing (a) N_2–CO_2 and (b) N_2–H_2O mixed gases.

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Influence of agglomeration of the glass set on the melting of sodium-calcium-silicate glass with increased content of substitute raw materials

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Keywords: glassy waste, Calumite slag, thermal analysis, agglomeration.

Currently, more and more attention is paid to the rational use of raw materials. Actions in this area include the elimination of various types of dust and dust materials from the production cycle. The batch of the glassware in the form of a dry and loose mixture always leads to the segregation of ingredients. Due to the different density and particle size of the raw material dusting occurs. The use of a compact glass set in the form of granules is advantageous in view of minimizing the delamination of raw materials and significant reduction of dusting. The thermal conductivity and improvement of the energy efficiency of the melt increases. The influence of sets of 60% of the colorless cullet and 15% Calumite slag treated as a raw material substitution on the process of batch melting was studied. The tested glass sets were compacted by mechanical compression. The research was conducted using, differential thermal analysis (DTA) and thermogravimetry (TG) based on a composition of model glass [wt.%]: 73.0% SiO_2, 1.0% Al_2O_3, 10.0% CaO, 2.0% MgO and 14.0% Na_2O. The influence of sulfate and multicomponent fining agent – a mixture of As_2O_3, Sb_2O_3, $NaNO_3$ in the proportions of 1 : 1 : 1 on the chemical reaction and phase transformation were tested. It was found that compaction of a loose glass set by pressing resulted in raising the temperature of all reactions related to the decomposition of carbonates. There is a decrease in the degree of decomposition, expressed by the amount of weight loss accompanying the given reaction stage in the glass set. This is due to the impeded release of CO_2 as a reaction product, when the set is compacted, its pressure (partial pressure in the pores) increases in the glass set.

Thermal decomposition of clusters and coordination polymers: reaction chemism and kinetic stability

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Keywords: Cluster compounds, inclusion compounds, decomposition processes, kinetic stability, non-isothermal kinetics

Hydrates of (MoVI MoV)-clusters are very complex compounds. Such cluster compounds includes water molecules not only as ligands, but as water nano-clusters. Cluster (H2O)100 are highly organized with three concentric shells spanned by 20, 20, and 60 molecules, respectively. Water nano-capsules itself are the essential part of the compound architecture stability. These water nano-capsules are under the pressure about 19 MPa, so they are really the ice–II. The formation of such complex compound from the aqueous solution is the formation of the bulky supramolecular inclusion compound, where the included water molecules support the whole structure stability [1–3].

There are no thermodynamically stable intermediate hydrates during the dehydration of Mo–cluster compounds, such as Na12[MoVI72MoV60O372L30(H2O)72].nH2O (n ≈ 300); L = glycine, valine, cysteine, asparagine [4]. The dehydration processes of these Mo–cluster compounds are processes with two parallel independent reactions: A → B; C → D (not parallel B ← A → C; and not consecutive A → B → C). These compounds decompose as two–phase systems, as if the coordinated water molecules and molecules from nano–capsules are removed from the complex structure independently. The water mass loss ratio for the first and the second dehydration reactions is m1 / m2 ≈ 1: 3.

Inclusion compounds on the basis of polymer metal–organic frames (MOF), synthesized in water solutions, usually maintain the stable crystal structure after the thermal dehydration (“activation”). Sometimes the crystal structure is unstable without the support of included water molecules and amorphisyses.

Thermal decomposition reactions and kinetic stability of the Sc–based coordination polymers and inclusion compounds were studied: [Sc2(H2O)2(fdc)3], [Sc2(dmf)2(H2O)2(pzc)3], ((CH3)2NH2)[Sc(H2O)2(fdc)2]·1.5CH3CN and [Sc2(dmf)2(H2O)2(pzc)3]·2H2O (fdc2– = 2,5-furandicarboxylate, pzc2– = 2,5-pyrazindicarboxilate). The stability of metal-organic frames is different: fdc-compound is stable up to ≈ 320ºC, but pzc-compound loses coordinated water and dmf molecules at 100–250ºC with the complete structure destruction. The inclusion fdc-compound begin to decompose at <100ºC and loses stepwise included CH3CN-molecules and coordinated water molecules. The inclusion pzs-compound loses stepwise both included and coordinated water molecules and decomposes at >250ºC. The kinetic stability of studied compounds is discussed.

Thermogravimetric measurements were carried out on a Netzsch thermal analyzer TG 209 F1; thermogravimetric curves were used for the kinetic studies, the heating rates were 5, 10 and 20 K min-1.

Acknowledgments

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Copper oxide-polymeric carbon nitride composite: a new class of catalyst for solid propellants

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Keywords: Polymeric carbon nitride, ammonium perchlorate, solid propellants

Sustainability has engaged the research community in search of new benign green catalysts for viable development. This quest has ended up in the re-invention of age old graphene like polymeric carbon nitride (gcn) as a new eco-friendly catalyst. The intrinsic features of gcn such as good surface area, tunable electronic properties, metal free nature, high electrical and thermal stability[1] and easy availability has already put gcn in the lime light as a potential candidate for various applications. Presence of $–NH/-NH_2$ groups in the tri-s-triazine units of gcn imparts a lewis base nature to polymeric carbon nitride. These features introduce gcn as an eco-friendly catalyst for the thermal decomposition of ammonium perchlorate (AP), a common oxidizer for composite solid propellants[2]. Since AP accounts for 60-70% of propellants, the thermal behaviour of AP directly affects the propellant performance[3]. In this work, leaf like nano copper oxide have been embedded on gcn sheets via sono-chemical approach with varying copper oxide content. X-ray diffraction analysis confirmed the formation of monoclinic phase of CuO and gcn. Morphology studies done using FE-SEM have conveyed the leafy structure of synthesized CuO which is in a nano regime. Transmission electron microscopy studies portray the silky structure of synthesized gcn nanosheets on which nanosized CuO with leaf like morphology were dispersed. The SAED pattern of the composite gives the polycrystalline nature of the synthesized composite with rings corresponding to both gcn and CuO. Thermal studies conducted using TGA and DSC has proven the catalytic activity of synthesized composite towards AP decomposition. Compared to pure AP, by the addition of 2wt% gcn/CuO, the two stage decomposition process has become single stage by lowering the decomposition temperature from 367ºC to 308ºC with almost complete decomposition. The better catalytic activity of the gcn-CuO composite may attribute to the inimitable surface structure of gcn favourable for $HClO_4$ diffusion via Lewis acid-base interaction[2] and presence of O^{2-}, a perfect proton trap for NH_4^+ on the surface of metal oxide[4].

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Kinetic modelling of coking coal fluidity development

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Keywords: coal, fluidity, modelling, kinetics

Coal plasticity is a phenomenon directly affecting creation of coke structure. It is very much time and temperature dependant transformation of coal matrix, which allows to change the physical phase from solid to liquid like within a certain range of temperature. Kinetics of this transformation is complicated if considering detailed coal chemical structure. In this work a macro kinetics approach was applied, which results in effective kinetic parameters, i.e. pre-exponential factor and activation energy. Coking process, particularly in a plasticization temperature range can be considered as a nonisothermal reaction at constant heating rate. Thus standard test for fluidity measurement was conducted at 3K/min temperature rise. Coal sample can melt steadily with the temperature increase achieving the maximum fluidity (Fmax). This takes place at tmax measured by standard Gieseler test. At temperature greater than tmax a plastic phase starts to turn intensively into solid phase by the domination of solidification reaction. According to the metaplast theory a depolymerisation of coal matrix leads to the liquid metaplast formation (P), which represents the part of coal. It is postulated that metaplast has its origin in a volatile matter content, and constituting a fraction of its content (M0). Considered temperature dependant coal fluidity (F) is proportional to the ratio of plastic phase (P) present at considered temperature to the content of solid phase composed of fixed carbon and ash (K) and still not plasticized metaplast (M) or already solidified plastic phase (S). This leads potentially to the development of two kinetic models. The first kinetic model is based on the assumption that the plasticization of coal and subsequent solidification is described by two independent reactions with the defined temperature range. The kinetic parameters can be computed knowing the value of M0 content, different for each coal, which was deducted experimentally running TGA pyrolysis tests within the plastic state temperature range.

The plasticization and solidification most probably takes place in the entire range of temperatures and for this reason a second model was developed expressed by reaction in series, which start since the coal begins to melt. In this case three nonisothermal kinetic rate equation can be formulated, with four kinetic parameters. This set of equations cannot be solved analytically because the variables are not separable. To find the solution the own procedure was developed, which assumes guess values of kinetic parameters and then it is possible to solve numerically the set of equations. Comparison of model results with experimentally calculated plastic phase content allows to finish computing conducted in a loop with properly stepwise adjusted kinetic parameters. The factorial design of four factors at two levels was applied for optimized procedure of kinetic parameters calculation.

The computation was conducted in MathCAD environment applying MinErr solver with respect to four kinetic quantities. Course of relative fluidity development was approximated by functions interp and cspline, which allow to interpolate real results with piecewise polynomial function. Computation of the set of differential equations was conducted applying rkfixed solver.

Experimental works were conducted with 15 coals of different origin. Tested coals were from Australia, USA, Canada, Poland and Czech Republic. The volatile matter content was in a range 15–32%, and it resulted in fluidity range from a few ddpm up to thousands ddpm. Experimental tests of fluidity were carried out using FRICO Gieseler plastometer. Samples for test were prepared as a routine sample of size distribution <0,425 mm, sample mass – 5 g. Temperature increase was typical – 3 K/min. TGA analysis was conducted applying LECO 501 analyser at the heating rate 5 K/min.

Catalytic and non-catalytic pyrolysis of nerium oleander

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Keywords: Nerium Oleander, pyrolysis, zeolite 5A and kinetic parameters

The choice of biomass for the production of biofuels via pyrolysis/gasification that is not consumed as a food product is important. *Nerium oleander* is a poisonous plant that is grown in arid and semi-arid regions throughout the year and is not consumed by humans and cattle. It is impossible to design and scaleup a pyrolysis reactor for biomass whose kinetic rate parameters are not known. The kinetic rate parameters, namely, order of the reaction, pre-exponential factor and activation energy depend on process variables such as heating rate, particle size, catalyst and mixing conditions in the reactor. In this work, the pyrolysis of stems and leaves of *Nerium oleander* was carried out using Thermogravimetric analysis with zeolite 5A catalyst and without catalyst in the temperature range of 25^{o}C to 700^{o}C, with different heating rates between 5^{o}C/min to 20^{o}C/min under nitrogen atmosphere. A constant biomass to catalyst ratio of 4:1 was used for all the studies involving the catalyst. Three different particle sizes namely, 1000, 500, and 125 microns were chosen for the study. Three degradation stages, attributed to hemicellulose, cellulose and lignin were observed under pyrolysis conditions, based on the degradation temperature. The number of degradation stages were not affected by catalyst. It was observed that, the range of degradation temperature with catalyst for all the three degradation stages was narrower when compared to without catalyst. The overall mass loss% with and without catalyst was observed to be the same. The kinetics parameters were determined using Coats-Redfern model, which was chosen based on the recommendations from International Confederation for Thermal Analysis and Calorimetry (ICTAC) for decelerating shape of the mass loss vs. time curve. The reaction order was found to be same for with and without catalyst. The pre-exponential factors for with catalyst was observed to be 1000 times higher than that of without catalyst. On the other hand, the activation energy for the catalyst was also observed to be 20-30 kJ/mol higher when compared to without catalyst. Though, the activation energy for biomass degradation with catalyst were higher when compared without catalyst, the average kinetic rate constant in the three degradation stages is also 10 to 1000 times higher for biomass degradation using catalyst than to degradation without catalyst. These large differences in kinetics parameters with and without catalyst suggest that, the reactions occurring during pyrolytic degradation of *Nerium oleander* in the presence of the catalyst are different from the reactions without catalyst. Further, the activation energies were affected by particle size without a catalyst, which was not the case in the presence of catalyst. This indicates that, the catalyst is more selective to pyrolytic reactions.

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Thermal decomposition kinetics of some aromatic azomonoethers; Part V. Influence of introducing a methyl rest to the benzyloxy group of BOPPD liquid crystal

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Keywords: azoic dyes, liquid crystals, kinetics, thermal decomposition

Azoic dyes are of large interest from the point of view of possible applications: dyes, liquid crystals as powders or thin films. Thermal analysis and kinetic studies of thermal induced changes of new compounds designed for temperature controlled applications is a real need and an advantageous pointer before trying to functionalize them; a novel class of azoic dyes, the azomonoethers, are valuable compounds that deserve our attention.

This study aims to investigate the influence of introducing a methyl rest to the benzyloxy group of BOPPD liquid crystal with the chemical names: 4-[benzyl(oxy)]azobenzene or 1-(4-(benzyloxy)phenyl)-2-phenyldiazene, to the thermal and kinetic stability. Because of the impossibility of evaluating the entire kinetic triplet $\{E, A, f(\alpha)\}$ that describes a physical or chemical transformation, from simple procedures like isoconversional methods, more sophisticated kinetic methods (Invariant Kinetic Parameters method, Perez-Maqueda *et al.* criterion or Master plot methods) were used. When several conversion functions may be situated on the same straight line and the correlation coefficients have high comparable values, the Perez-Maqueda *et al.* activation parameters should be compared with the invariant ones. If after using all known conversion functions there is no joint straight line to be found, then Master plot methods should be used. The kinetic analysis was performed by means of our software TKS-SP. A step by step visual fit of the normalized experimental data – $(d\alpha/dt)/(d\alpha/dt)_{max}$, by adjusting the $[f(\alpha)\cdot g(\alpha)]/[f(\alpha_{max})\cdot g(\alpha_{max})]$ master equation with the appropriate selected conversion degree and conversion function, is the main advantage in determining the true kinetic model for each constant heating rate experiment.

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TGA and kinetic studies of photo-degradation of copper surfactants derived from various oils

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The copper surfactants derived from various edible (Mustard and Soyabean oils) and non-edible oils (Neem and Karanj oils) and their complexes with nitrogen and sulphur containing ligands such as 2-amino-6-methyl-benzothiazole have been synthesized and studied for their structural aspects, which were confirmed using various techniques like IR, NMR and ESR spectroscopy. Thermo Gravimetric Analysis (TGA) has been used to study the thermal decomposition of copper surfactants complexes to evaluate their energy of activation and various thermodynamic parameters i.e. Gibbs free energy, enthalpy, entropy have been calculated. Copper surfactant sand their benzothiazole complexes were studied to test the validity of various equations namely Freeman Carroll, Coats – Redfern, Horowitz – Metzger, Broido, and Piloyan -Novikova related to thermal degradation.

In the present investigation photocatalytic degradation has been applied for degradation of copper surfactants derived from various oils. The degradation was carried out by irradiating the aqueous solutions of copper surfactants containing ZnO with UV. In this technique a semiconductor ZnO is used which is non -toxic in nature. The rate of reaction was estimated from residual concentration spectrophotometrically by measuring the absorbance of the reaction mixture at definite time intervals. Different parameters such as the concentration of surfactant (0.4-0.96 g l^{-1}), amount of semiconductor (0.01-0.06 g), light intensity (26-54 mWcm^{-2}), effect of solvent polarity (20-80%) and time period for degradation (0-18 h) were varied to achieve the optimum rate of photo degradation. The observations revealed that both copper surfactants were degraded successfully by using ZnO under UV. The disappearance of copper surfactants follows a pseudo-first-order kinetics according to the Langmuir–Hinshelwood (L–H) model. A tentative mechanism has been proposed for the photo degradation of copper surfactants. Thermal degradation of solid components will be a good and significant method for the removal of the pollutant from the environment. The present study will play an important role in the field of environmental chemistry and biochemistry.

Importance of induction periods in the prediction of material lifetimes

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Keywords: non-Arrhenian temperature functions, extrapolation, degradation, induction period

Processes occurring in the condensed phase very often exhibit an induction period (IP) where seemingly no chemical reaction takes place. In fact, IP is a preparatory stage during which the reactive species accumulate in the sample. Theory and application of induction periods were described in our previous paper [1].

The rate of degradation processes under application conditions is usually too slow to be measured. To estimate the stability of materials, a sample is mostly subjected to an accelerated test where heating is the most common means of accelerating the process. The principal goal of stability studies is to extrapolate the kinetic data, obtained from accelerated stability tests, to the application conditions. The extrapolation to lower temperatures is almost exclusively carried out using the Arrhenius temperature function; however, indications are accumulating that the Arrhenian extrapolation leads to overestimation of the material stability [2]. In this contribution it will be shown that the differences in predictions for the Arrhenian and non-Arrhenian temperature functions is brought about predominantly by the differences in IP estimations. After terminating IP, the course of the degradation kinetics is practically identical for all the temperature functions employed. This finding agrees with the equivalence of the Arrhenius and non-Arrhenian temperature functions in the temperature range of measurement [3].

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Application of fractal kinetics on non-isothermal dehydration, dehydroxylation, and degradation of fullerol

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Keywords: fullerol, dehydratation, dehydroxylation, kinetics, fractal kinetics

Fullerols are derivatives of fullerenes with hydroxyl group on their surfaces. Due to the many of extremely important properties: radical scavengers, antioxidant, antimicrobial, anti-cancer and catalytic activity and strong electron affinity, etc. [1], fullerols found its application in a wide spectrum of scientific disciplines, of which one of the most important is in biomedical sciences [2]. Thus, understanding of interactions between fullerol molecule and water and other biofluids is of the great significance. On the other side, since physical, electronic and functional properties of fullerols are strongly dependent on number of hydroxyl group [3]. Having this in mind, our objective is to thoroughly investigate the non-isothermal kinetics of fullerol dehydration and dehydroxylation. Sample of fullerol was synthetized and characterised by various techniques. It was established that fullerol sample contains 24 groups on its surface. Non-isothermal thermogravimetric curves in temperature range from 423 K to 853 K has been recorded at different heating rates in interval from 5 K min^{-1} to 25 K min^{-1}. Thermogravimetric curves were differentiated and peak deconvolution were used in order to separate reactions and processes which occurs during thermal treatment. Complete thermogravimetric curves can be deconvoluted by three Fraser-Suzuki function which correspond to dehydration, dehydroxylation, and degradation of residue. All curves are further fitted by equation characteristic for the Brouers and Sotolongo-Costa model of fractal kinetics [4]. Dependences of effective rate-dependent coefficient on temperatures are calculated for dehydration process and dehydroxylation and degradation reactions at all heating rates using equations derived within framework of Brouers and Sotolongo-Costa model of fractal kinetics. Values of activation energy for dehydration, dihydroxylation, and degradation of fullerol were calculated from the dependences of rate constant on temperature using Arrhenius equation, as well as by the isoconversional method. Differences between these two approaches were discussed. Finally, activation energy distribution functions were calculated for all reactions and processes. From the obtained results were used to analyse changes in water structure during fullerol dehydration, as well as in fullerol structure during dehydroxylation.

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Non-isothermal kinetics: best fitting empirical models instead of model-free methods

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Keywords: Non-isothermal reaction kinetics, isoconversional, empirical kinetic models, method of least squares, combustion, gasification

In thermal analysis most non-isothermal kinetic works use the so-called model-free methods which are based on the equation $d\alpha/dt = A(\alpha)f(\alpha)\exp(-E(\alpha)/RT)$ (1)

Here α is the reacted fraction while $[A(\alpha)f(\alpha)]$ and $E(\alpha)$ are empirical functions. The term “model-free” is misleading because Eq. (1) itself is a model. The name “isoconversional kinetics” is more correct [1]. The $E(\alpha)$ values obtained this way vary between 10 and 1300 kJ/mol in the literature of the biomass materials [2]. Accordingly, the model-free methods do not find the “true” activation energies for complex reaction mechanisms; their results can only be regarded as empirical models. A further problem is that the available model-free methods aim at relatively simple procedures instead of finding a best fit between the predicted values and the observed data. A recent work [2] proposed true least squares evaluations by Eq. (1). For this purpose $[A(\alpha)f(\alpha)]$ and $E(\alpha)$ are described by simple but versatile empirical functions which contain adjustable parameters. The parameters are determined by the method of least squares: such values are searched which give the best fit for the DTG curves of the available experiments. The evaluations are based on the simultaneous evaluation of experiments with linear and non-linear temperature programs. Modulated, stepwise, and constant-reaction rate (CRR) experiments can also be used in the evaluations. It turned out that there is a particularly strong compensation effect between $[A(\alpha)f(\alpha)]$ and $E(\alpha)$, meaning that Eq. (1) is ill-posed from a mathematical point of view. Accordingly a particular care is needed in the evaluation to find such $E(\alpha)$ functions which are in a physically meaningful range but still approximate well the experimental DTG curves [2].

The present lecture summarizes the above results and extends the evaluations to such type of reactions which have not been treated in reference [2]. Among others the combustion and gasification of biomass chars will be examined.

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Pyrolysis characteristics and kinetics analysis of abalone shell

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Keywords: abalone shell, aalcination, phase change, physiochemistry, antioxidant activity

Abalone shell (AS) is a valuable Chinese tradition medicine with great potential in the treatments of various diseases. Herein, the thermal stability of AS was detected by thermogravimetry analysis. It was verified the pyrolysis of AS containing three stages, water loss (room temperature to 129 ºC), phase transition from aragonite to calcite (129 ºC to 571 ºC) and decomposition (571 ºC to 767 ºC). The organic species in the shell controls the crystallization and transformation of CaCO3. Kissinger– Akahira– Sunose model was then applied to calculate the average activation energy in the heating process, which was 178.628 kJ/mol and lower than that of the raw material. Moreover, the physicochemical properties of the calcinated AS were deeply investigated by spectroscopy technology. The enhancement of the characteristic peak at 875 cm-1 in FTIR indicated the polymorph transition of CaCO3 in calcination, which was further confirmed by SEM, EDS and XRD measurements. The study provide the guidelines for the pretreatments of abalone shell for pharmaceutical usage.

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Isoconversional cure kinetics of a novel thermosetting resin based on linseed oil

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Keywords: bio-based thermoset, isoconversional cure kinetics, induction period, point of gelation, multi-frequency dynamic tests

The purpose of this work was to analyse the thermal cure kinetics of a novel bio-based thermosetting resin system which was designed to cure at moderate processing temperatures (max. 60 °C). Linseed oil was epoxidized first, acrylated afterwards and functionalized with maleic anhydride, which transformed the vegetable oil into a thermosetting resin that curing mechanism was similar to an unsaturated polyester resin. This bio-based resin (MaAELO) was mixed with styrene as reactive diluent in the proportion 2:1 and cured by adding 2 wt.% of peroxide (MEKP) and 1 wt.% of Manganese based accelerator DriCAT 2700F (Dura Europe, Spain) to the mixture. The resin mixture was measured isothermal (40–60 °C) with a Mettler-Toledo (Greifensee, Switzerland) 822e DSC. In a 2nd DSC run each sample was measured again at 5 °C/min to determine the residual cure enthalpy. The degree of cure in the course of time, α(t), was calculated as ratio of partly integrated cure enthalpy to the total cure enthalpy, Htot. The apparent activation energy as function of cure conversion, E(α), was derived from isothermal α(t) curves by applying the integral isoconversional kinetic analysis (ICKA) method of Vyazovkin in its advanced form (VA) [1] and again by applying the differential ICKA method of Friedman (FR) [2]. For both methods, E(α) was utilized to determine the pre-exponential factor, A(α), by using the compensation effect [3]. Once E(α) and A(α) were evaluated in a model-free way it was able to reconstruct the reaction model f(α). Both sets of parameters were validated by comparing α(t) of isothermal DSC experiments with predicted α(t)-values. In this context the prediction with all three parameters was compared with the prediction based on E(α) alone. The induction period, ti, before the cure started was plotted as ln(ti) against 1/T to calculate the activation energy, Eind, by linear regression [4]. Samples of cured resin (cured at 25 °C for 72 h without and inclusive tempering at 80 °C for 8 h) were measured at 10 °C/min with a Mettler Toledo (Greifensee, Switzerland) TMA/SDTA 840 to determine the glass transition temperature, Tg. The thermal cure was further analysed by rheology with a Physica MCR 101 (Anton Paar GmbH, Graz, Austria) between parallel plates in dynamic oscillatory mode with simultaneous frequency sweeps (deformation=3%; frequencies=5, 10, 20, and 30 s^{-1}) at 45 and at 50 °C. The measurements were stopped when the resin reached the G’-G’’ crossover point at highest frequency. The partially cured samples were measured again by DSC at 5 °C/min to determine the degree of cure at gelation, αgel, and at respective crossover points. Htot at isotherms was around 280 J/g. Both methods, VA and FR, led to similar kinetic parameters. E(α) was kept nearly constant around 25 kJ/mol at $\alpha < 50$ %, and increased significantly afterwards up to 65 kJ/mol. E(α) was used to predict α(t) for five isotherms. Obviously the prediction was very precise and as accurate as the prediction with the whole set of all three parameters. In order to model the induction period, Eind was calculated (60 kJ/mol) from the slope of linear regression (R^2=0.96). The resin reached gelation very soon, namely at α<5 %. With increasing frequency the crossover points shifted to longer periods, but maximal 120 sec after gelation. By TMA analysis, the Tg of the cured resin was determined at 46 °C. Under the chosen tempering conditions, the Tg increased up to 55 °C.

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Life sciences

Blood plasma survey signals after surgery

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Keywords: surgery, extension, blood plasma, DSC, thermoanalysis

It is a well-known fact that the extension of the surgical intervention influences both the success and time of the patient's recovery, the size of the blood loss, ie, overall the patient's surgical loading. Itself the disease determines extent of surgical procedure (minor, medium or major surgery), which affects the risk and frequency of complications. Previous works have contributed to the validation of Differential Scanning Calorimetry (DSC) as a potential non-invasive tool for diagnosing and monitoring several illnesses. Hence, the main goal of this study was to measure the effect of each surgical intervention on its own to blood plasma composition. Peripheral venous blood samples were collected from patients who underwent minor, medium and major surgical interventions (n=10 in each group). According our DSC data, from the thermodynamic parameters the thermal transitions and calorimetric enthalpy corresponding to the size of surgery (operation time, length of incision, etc.). This examination has shown that surgical intervention alone influences for the composition of plasma proteins, which should be always considered during evaluation of DSC results in any surgical study.

Materials science

A scientific career viewed through publications in the journal of thermal analysis and calorimetry

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Keywords: Feed-back, Monte Carlo simulations, Kinetics, Photo-mechanical effects, High-pressure, Crystalline amino acids and peptides, Pharmaceuticals, Mechanochemistry, Freeze-drying

The Journal of Thermal Analysis and Calorimetry (JTAC) celebrates its 50th Anniversary. Almost 30 years of my scientific career are closely related with this journal. Amazingly, as I can see now retrospectively, whenever I started a completely new research direction, JTAC was the only journal that was open to publish the first results of this work. They were not very well understood at that time by most other researchers and were not accepted either to be published in other journals, or to be presented at a conference. Time has shown to which extent the JTAC was right in taking the risk of publishing something absolutely new. Each of these new trial directions transformed with years into a mainstream followed by many researchers throughout the world. These first papers accepted by the JATC remain my most cited papers. My presentation at the 2019 Meeting is a tribute to the JTAC, a journal that could recognize the novelty of a research long before any other journal did.

I give an overview of the early work in the field of solid-state kinetics, when Monte-Carlo simulations were used to model the feed-back phenomenon and its role in determining the rate and spatial propagation of solid-state reactions. Computer modeling of solid-state reactions was rather rare in the 1980s, and it did not seem to be directly related to thermal analysis. Still, the summary of these pioneering results was accepted to the JTAC [1]. It took several decades before a similar research was published by someone from a new generation [2]. Another pioneering work that was also discussed in [1] was related to the photomechanical effects in the crystals of some coordination compounds that were elastically (reversible) bending on irradiation with visible light. First observed by us in the 1980s [3], the phenomenon became very widely studied from the 2000s [4]. The research in this direction made it possible nowadays to relate the macroscopic crystal deformation with the kinetic constants, quantum yields and the activation energies of the elementary stages of the solid-state photochemical reactions [5]. Another really novel study was the discovery of the pressure-induced polymorphic transformations in crystalline pharmaceuticals [6]. The JTAC was the first journal that has accepted these results for publication, when there were practically no similar papers published elsewhere. It is this research direction that has become extremely popular since that time and lead to a new method of the control of polymorphism of drugs [7]. For many years the JTAC was also the journal where the results of detailed systematic studies of the polymorphism of amino acids and dipeptides, their heat capacities and phase transitions were published, starting with glycine [8]. The last but not least new research direction is solubilization of drugs by mechanochemical [9] and cryogenic [10] technologies. The latter can be also used to prepare inhalation powders [10].

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Thermal behavior of ni-zn ferrite nanoparticles embeded in silica and pva matrix

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Keywords: thermal analysis, sol-gel, nickel-zinc ferrite, nanoparticle, thermal decomposition products

Mixed Ni–Zn ferrites are of special interest due to their remarkable properties such as high resistivity, saturation magnetization and mechanical hardness, very good chemical stability and low dielectric losses that makes them suitable for information storage systems, high frequency circuits, high-quality filters, magnetic fluids, sensors and medical diagnosis devices [1-4]. The paper presents the synthesis of Ni0.4Zn0.6Fe2O4 nanoparticles embedded in SiO2, PVA and hybrid PVA-SiO2 matrices by a modified sol-gel method. The influence of matrix type on the formation of Ni-, Zn- and Fe-succinate precursors and their decomposition into Ni0.4Zn0.6Fe2O4 within the pores of SiO2, PVA or PVA-SiO2 matrices was also investigated. Transmission Electron Microscopy of synthetized samples revealed spherical shape ferrite particles. The decomposition processes, formation of crystalline phases and mass changes during gels annealing at different temperatures were assessed by thermal analysis. The formation/decomposition of Zn-, Ni- and Fe-succinates and the formation of the silica/PVA matrix were studied by Fourier-Transform Infrared (FT-IR) spectroscopy, while the formation of main (ZnFe2O4, NiFe2O4) and secondary phases were confirmed by X-ray diffraction analysis.

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The study of the inductive heating of the molybdenum sheet

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Keywords: molybdenum sheet, inductive heating, field shaping, finite element method

This paper deals with the development of the simulation model of the inductive heating of the molybdenum sheet. The main issue is the development of a precise simulation model of thick molybdenum sheet, which will consider possibilities of inductive heating within its volume for the required modification purposes of its geometric shape (e.g. design of high-performance thermal shells). The proposed model is created in COMSOL environment and it is compared to a measurement. The proposed model is used to determine the optimal shape of the magnetic element (ferrite) of inductive heating system, through which the electromagnetic field is enclosed trough molybdenum sheet. The material parameters of the ferrite are reconfigurable so the different material for magnetic circuit can be studied. The influence of the coil shape on the inductive heating system properties is studied as well. Next part of this publication is dedicated to the acquisition of thermal-frequency characteristic for a given shape of the magnetic element of the heating system. The result of the proposed model can be used for optimization of heating element shape as well as for optimization of the control algorithm of inductive heating system based on acquired frequency characteristic.

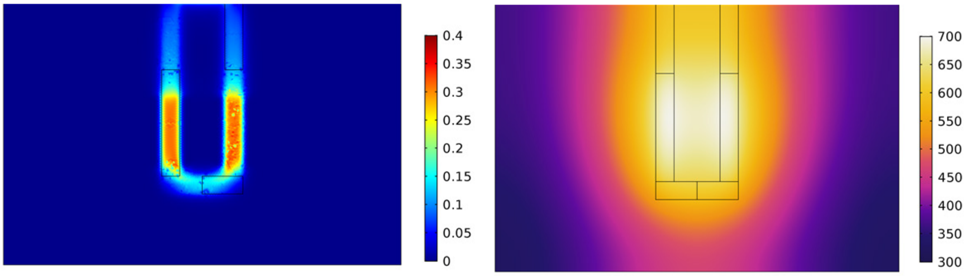

Fig.1. Example of simulation - Volumetric loss density [W/mm^3] (left), Temperature distribution [°C] (right)

Acknowledgments

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Thermal effect on the superficial properties of solid substrates and determination of transition temperatures of polymers by inverse gas chromatography

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Keywords: Specific enthalpy; Lewis acid and base constants; Polymers; Oxides; infinite dilution.

Inverse gas chromatography at infinite dilution was used in this paper to characterise the superficial and interfacial properties of solid substrates as oxides, polymers or polymers adsorbed on oxides. We applied this technique in order to determine the change, as a function of temperature, of the properties of some polymers and to study the second order transitions of such polymers adsorbed on oxides. Probes of known properties are injected in the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between the organic molecules and the solid, if we suppose that there is no interactions between the probe molecules themselves.

We studied the surface properties of oxides such as MgO, ZnO, SiO2, TiO2, Al2O3 and porous materials, and the transition phenomena in polymers such as PMMA and poly(□-n-alkyl) methacrylate adsorbed on silica or alumina in their bulk phases. In the case of polymers (in bulk phase or adsorbed on silica or alumina), we showed that the evolution of RTlnVn obtained by IGC as a function of 1/T for different n-alkanes, allowed to determine with a good accuracy the transition temperatures. T□□, the transition temperature relative to □-relaxation, Tg, the glass transition temperature and Tl,l the liquid-liquid transition temperature or order-disorder transition were detrmined.

Measurements of retention volumes of molecules were carried out with a classical Chromatograph equipped with a flame ionisation detector of high sensitivity. The retention data were obtained with a stainless steel column of length 15 cm to 30 cm and 2 mm internal diameter packed with 1 to 2 g of polymer or oxide powders.

In this paper, we used oxides such as MgO, ZnO, SiO2, TiO2, Al2O3 and porous materials; and polymers such as PMMA and poly(□-n-alkyl) methacrylate in bulk phase or in adsorbed state.

The acid-base constants were calculated for many solids: Monogal, MgO, ZnO, carbon fibers and porous materials. On the other hand, we proposed a new relationship to describe the acid-base properties of solids and adding a new parameter K reflecting the amphoteric character of the solid and correcting the classical relationship previously used to obtain the acid-base constants of solid surfaces. The determination of acid-base properties in Lewis terms as the acidic (KA) and basic (KD) superficial characteristics of the solid substrates proved an effect of the temperature on these values and allowed to correct the classical relationship by the introduction of a third new constant (K) to take into account the amphoteric character of the solid. Results obtained improved the understanding and the knowledge of surface properties of some solid substrates and gave a new contribution in the characterization of acid-base properties of solid surfaces. A new relationship was proposed:

(–□Hsp) = KA.DN + KD.AN – K. AN.DN (3)

Where the (-□Hsp) the specific enthalpy, and DN and AN are respectively the electron donor and acceptor numbers of electrons of the polar molecules used in this study.

Evaluation of stability of Pr2-xNdxNiO4+δ by thermogravimetry under various oxygen partial pressures

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Keywords: Pr2-xNdxNiO4+δ, thermogravimetry, van’t Hoff plot, Jander model

$Ln_2NiO_{4+\delta}$ (Ln: lanthanoid) with K_2NiF_4-type structure has high mixed ionic and electronic conductivity and attracts interest as new cathode materials of solid oxide fuel cells. Among $Ln_2NiO_{4+\delta}$, $Pr_2NiO_{4+\delta}$ is most expected because it shows the highest δ due to higher valence of Pr than other lanthanoid. However, decomposition under high oxygen partial pressures, $P(O_2)$, described as follows should be prevented for practical application.

$$3Pr_2NiO_{4+\delta}(s) + 0.83O_2(g) \leftrightarrow Pr_4Ni_3O_{10+\delta'}(s) + 2PrO_{1.83+\delta''}(s) \qquad (1)$$

It was reported that partial substitution of Nd for Pr was effective to improve stability under high $P(O_2)$; however, temperature and $P(O_2)$ region where $Pr_{2-x}Nd_xNiO_{4+\delta}$ is thermodynamically stable has not been quantitatively clarified. Kinetics of reaction (1), which is also important information for application, has not been reported either. In this study, thermodynamic and kinetic stability of $Pr_{2-x}Nd_xNiO_{4+\delta}$ were evaluated by thermogravimetry under various $P(O_2)$.

$Pr_{2-x}Nd_xNiO_{4+\delta}$ was prepared by the Pechini method. The obtained specimens were confirmed to be a single phase with K_2NiF_4 structure. In order to evaluate decomposition behaviour, thermogravimetry was performed with TG8120 (Rigaku Co., Ltd.) from room temperature to 1200°C under various $P(O_2)$. About 50 mg of the specimens was loaded in Pt pan and the heating rate was 3 °C/min. The $P(O_2)$ was controlled by mixing flow rate of O_2 and Ar and monitored by zirconia O_2 sensor set at downstream of the apparatus.

Fig. 1 shows TG curves of $Pr_2NiO_{4+\delta}$ under various $P(O_2)$. Differential curves of weight variation (DTG) are also depicted. For $P(O_2)$ of 0.5 bar or more, weight increase due to reaction (1) was observed around 725 °C. Sudden weight decrease, which was identified as reverse reaction (1), was detected at 1073 °C under $P(O_2)$ of 1.0 bar. The temperature was regarded as apparent equilibrium temperature of reaction (1) at $P(O_2)$ of 1.0 bar. With decreasing $P(O_2)$ to 0.5 bar, the apparent equilibrium temperature decreased. At $P(O_2)$ of 0.2 bar, weight increase owing to decomposition was not observed, indicating that reaction kinetics was so low that decomposition was not observed in this condition. In TG curves of $Pr_{2-x}Nd_xNiO_{4+\delta}$ with x=0.25 and 0.50, sudden weight changes identified as reaction (1) were also observed. Fig. 2 shows van’t Hoff plot of equilibrium

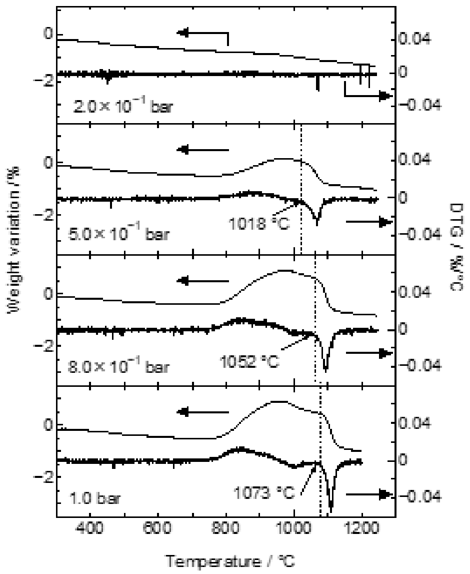

Fig. 1 TG-DTG curves of $Pr_2NiO_{4+\delta}$ under various $P(O_2)$

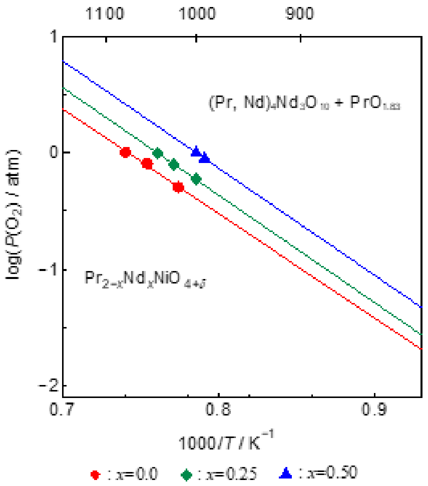

Fig. 2 van’t Hoff plot of equilibrium reaction (1)

reaction (1) evaluated from TG-DTG curves. Temperature and $P(O_2)$ range where $Pr_{2-x}Nd_xNiO_{4+\delta}$ is thermodynamically stable expanded slightly with increasing Nd content up to 0.5. With increasing x of 0.75 or more, decomposition reaction was not observed by TG, indicating x more than 0.75 was necessary to obtain thermodynamically stable specimens as SOFC cathode material.

Phase evolution and optical properties of Eu-doped at Sr and Sn-site in Sr_2SnO_4 Layered Perovskite

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Keywords: Layered perovskite: Sr_2SnO_4 ; Rietveld refinement; Raman Spectroscopy; Photoluminescence spectroscopy

The structural and emission analysis of Sr_2SnO_4, $Sr_{1.99}Eu_{0.01}SnO_4$, and $Sr_2Sn_{0.99}Eu_{0.01}O_4$ were analysed in detail. The thermal analysis of the mixture of raw materials reveals the reaction among the raw materials takes place around 1000°C. The reaction mechanism path for one representative sample was investigated in detail. The Reitveld refinement of the X-ray diffraction data shows the solubility of Eu on both site of Sr_2SnO4. Higher crystallite size and lattice strain were observed for $Sr_{1.99}Eu_{0.01}SnO_4$ than $Sr_2Sn_{0.99}Eu_{0.01}O_4$, because Eu^{3+} acts as donor at Sr^{2+} site while as acceptor at Sn^{4+} site. Absences of any band associated with raw materials in Raman spectrum also confirm the monophasic nature of the sample. The photoluminescence (PL) spectra of Eu-doped samples exhibits strong peak at 612 nm ascribed to electric dipole transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} shows higher peak intensity and width for $Sr_{1.99}Eu_{0.01}SnO_4$ than $Sr_2Sn_{0.99}Eu_{0.01}O_4$.

The study of bitumen's microstructure by modulated differential scanning calorimetry

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Keywords: bitumen, microstructure, modulated differential scanning calorimetry

Bitumen is widely used in various fields of the economic branch depending on the composition and structure. In this regard, the study of the structure of the bitumen is a very important task. One of the methods of studying the structure of bitumen is a modulated differential scanning calorimetry (MDSC). MDSC curves of bitumen show the different thermal events that occur in the bitumen as the temperature changes (glass transition, cold crystallization, recrystallization, melting) and provide the capability for their separation and identification [1]. In the presented work the MDSC is used for study of structure of model bitumens. Model bitumens were prepared by mixing saturated (including macrocrystalline paraffins) and aromatic hydrocarbons, resins and asphaltenes in different ratios. The saturated hydrocarbons content varied from 0 to 50% mass, macrocrystalline paraffins – from 0 to 14% mass, aromatic hydrocarbons – from 0 to 50 % mass, asphaltenes – from 15 to 25% mass.

The following features of thermal behavior of model bitumens in temperature interval from –50 to 90 °C were established, and the following conclusions regarding bitumen structure were made.

1. For the model bitumen, containing aromatic hydrocarbons, resins and asphaltenes, there is only the glass transition effect in the temperature range from –45 to –16 °C on the heat flow curve. Thus, the bitumen of such composition has amorphous structure.

2. For model bitumen, containing saturated (without macrocrystalline paraffins) and aromatic hydrocarbons, resins and asphaltenes there are the glass transition effect and the peak of cold crystallization on the heat flow curve. It is assumed that such bitumen contains weakly-ordered phase (mesophase), formed by low-molecular weight saturated hydrocarbons.

3. For model bitumen, containing saturated (with macrocrystalline paraffins) and aromatic hydrocarbons, resins and asphaltenes, the heat flow curve shows the thermal peaks of cold crystallization (–35 ÷ –10 °C), melting (from 0 to 50 °C) and recrystallization (25 ÷ 35 °C). At negative temperatures (–50 ÷ –25 °C) in bitumen there are several types of amorphous phases, formed by saturated and aromatic hydrocarbons, resins and asphaltenes, and the mesophase, formed by saturated hydrocarbons. At heating the partial devitrification of saturated and aromatic hydrocarbons occurs and a possibility of their ordering appears. In the temperature range from 0 to 50 °C the destruction of this ordered phase occurs. It leads to an increase in the mobility and recrystallization of high-molecular weight hydrocarbons in range of 25 ÷

35 °C. In bitumen with the maximum content of macrocrystalline paraffins the melting peak has the highest magnitude.

4. The content of asphaltenes in model bitumen effects on the width of the low temperature glass transition effect and the magnitude of the recrystallization effect. Besides, in the model bitumen with a high content of asphaltenes the high-temperature glass transition (70 ÷ 90°C) appears. This indicates that in bitumen of such composition there is the high-temperature resin-asphaltene mesophase.

Acknowledgments

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Mechanical properties of hybrid woving roving and chopped stand mat glass fibers reinforced polyester composites

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In high-performance composite manufacturing industries, glass fibers is one of the most important reinforcements with excellent mechanical properties. The aim of this study is to compare the mechanical properties of two types of fiber glass reinforced polyester composites. Woving Roving Fiber (WR) and Chopped Stand Mat Fiber (CSM), for different layers (2, 4, and 6) respectively, were used to fabricate the composites by hand lay-up method. Moreover, hybrid mixing of the two types of fibers was also fabricated for (2, 4, and 6) layers. The mechanical properties included tensile, impact, flexural, and Rockwell Hardness. Also, scanning electronic microscope (SEM) was used to examine the fracture failure of the composites after the tensile test. The results show that all the mechanical properties of the composites improved by increasing the number of layers of the glass fibers. The composites which reinforced with fiberglass type (WR) have better tensile strength while the hardness and flexural strength improved when reinforced with the fibers type (CSM). However, the hybrid composites dominate the best mechanical properties. The morphology analyses were supported the mechanical results.

Isothermal martensitic transformations in NiTi-based shape memory alloys: Kinetics and strain behaviour

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Keywords: isothermal martensitic transformation, NiTi-based shape memory alloys, kinetics, shape memory effect

The thermal elastic martensitic transformation which is responsible for the shape memory effects was discovered in 1949 by Acad. G.V. Kurdumov and Prof. L.G. Khandros. From that time, it is believed that this transformation is characterized by athermal kinetics and does not occur during isothermal holding. At the same time, last decade it was found that in some cases, the martensitic transformation in NiTi-based alloys might take place during isothermal holding of the sample at temperatures within temperature range of the athermal forward martensitic transformation or even at temperatures which were higher than the start temperature of the athermal forward martensitic transformation (Ms) that was measured by differential scanning calorimetry (DSC). The aim of the present work is to study the kinetics of this new type of the transformation in the NiTi-based shape memory alloys to clarify the nature of this phenomenon and to first observed whether this type of the transformation induced the strain variation as it was found during the athermal martensitic transformation or not.

To study the kinetics of the isothermal martensitic transformation in the NiTi-based alloys, the DSC was used and the volume fraction of the alloy that transformed to the martensite at a constant temperature was estimated as the ratio of the enthalpy of the reverse transformation that occurred on heating after isothermal holding to the enthalpy measured on heating after athermal martensitic transformation took place on previous cooling. The binary Ni50Ti50, Ni51Ti49, ternary Ti50Ni25Cu25, quaternary Ti40.7Hf9.5Ni44.8Cu5, Ti40.7Hf9.5Ni41.8Cu8, Ti40.7Hf9.5Ni39.8Cu10 alloys were used in the study. It was found that isothermal forward martensitic transformation took place in the samples with non-stoichiometric composition (Ni51Ti49, Ti40.7Hf9.5Ni44.8Cu5, Ti40.7Hf9.5Ni41.8Cu8, Ti40.7Hf9.5Ni39.8Cu10) and never been observed in stoichiometric Ni50Ti50, and Ti50Ni25Cu25 alloys. The detail study of the transformation kinetics in Ti40.7Hf9.5Ni44.8Cu5 and Ni51Ti49 alloys showed that the isothermal martensitic transformation occurred on heating within and outside the temperature range of the athermal forward martensitic transformation. The maximum volume fraction of the martensite that appeared during the isothermal holding depended on the holding temperature and the maximum value was observed if the holding took place at the Ms temperature. This value was less than 100% and depended on the alloy composition. For instance, in the Ti40.7Hf9.5Ni44.8Cu5 alloy 80% of the martensite may appear during holding at the

Ms temperature whereas, only 45% of martensite formed in the Ni51Ti49 alloy at the same conditions. A new concept of the realization of the isothermal martensitic transformation in the non-stoichiometric NiTi-based alloys was proposed which showed that the nature of this phenomenon was related to the formation of the strain nanodomains due to the existence of the substitutional atoms in the NiTi matrix.

To study whether the isothermal martensitic transformation induces the strain variation as it is observed during athermal transformation, the isothermal martneisitc transformation is realized in the Ti40.7Hf9.5Ni44.8Cu5 and Ni51Ti49 samples under a constant load. It was first observed that the formation of the isothermal martensite in the NiTi-based alloys under a stress was accompanied by the strain variation that was fully reversible on further heating. An increase in stress that acted during holding increased the strain variation and changed the kinetics of the isothermal transformation.

Acknowledgments

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Inverse determination of experimental heat flux through a composite material wall exposed to kerosene/air flame

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Keywords: composite material, experimental and numerical study, heat flux estimation, inverse method

Nowadays, composite materials are getting more and more common in most industrial applications, due to their lightness. Indeed, composite materials offer the opportunity to produce lightweight structures leading to low fuel consumption; which explains their large use potential. However, their fire behaviours have to be checked to prove they follow aviation regulations. In this perspective, good comprehension of composite material behaviour facing high fire stress is required. Otherwise, the composite materials may get perforated due to huge fire stress, conducting to fire propagation in other compartments. The present work consists of an experimental study in conjunction with a numerical one to address the real heat flux received by the plate to clarify the exact conditions undergone by the material when it degrades itself. The developed experimental setup is a NexGen kerosene-fuelled burner. The flame temperature is 1100 °C and the heat flux is 110 Kw/m^2. These conditions represent the flame characteristics defined in the ISO 2685 standard and in AC 20-135 established by the Federal Aviation Authority (FAA). The burn-through resistance and the thermal behaviour of a plan of composite material is investigated. The real heat flux received by the material at the front face affected by the flame is determined. The heat flux density is estimated using the Function Specification Method (FSM) which is a heat conduction inverse method.

To estimate the transient heat flux crossing the composite material plate, variational formulation of 1D inverse heat conduction problem is considered. The problem is to find the boundary at the front face imposed by the flame for which temperature histories computed from the mathematical model at the sensor's locations would be close to measured temperature. The concept of this method consists of minimizing the residual function between measured and estimated temperatures, by direct solution of 1D heat conduction equation using finite difference method. The combination of experimental measurements and inverse approach allows quantifying the net heat amount transferred from the flame to the composite material plate, especially when the accessibility to such thermal condition is constrained. The experimental temperature measurements are used as initial conditions in the numerical heat flux determination. Subsequently, they are confronted to temperatures estimated numerically the estimated ones and the heat flux density which crosses the specimen wall is determined. An accurate estimation of the heat flux across the composite material wall could decrease prediction errors of numerical results obtained by computation codes.

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Influence of crystalline and amorphous phosphate phases on electrical properties and chemical stability of BaCe0.9Y0.1O3-δ protonic conductors

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Keywords: protonic conductors, glass-ceramic composite, optimization of preparation method

Complex oxides with a perovskite structure of the general formula ABO3, in particular BaCe0.9Y0.1O3, exhibit proton conductivity at high temperatures [1]. Unfortunately, the basic problem of this compound is low chemical stability, especially in atmospheres containing CO2 and H2O what as reported e.g. in [2]. One of the ways to improve the properties of materials based on the BaCe0.9Y0.1O3 (BCY) is the modification of an intergranular region possible e.g. via preparation of composite materials [3]. The purpose of the presented work was to determine the effect of introducing an additional phases in the form of barium phosphate and glass [4] with a chemical composition similar to the composition of the matrix material on electrical properties and chemical stability. The obtained selected materials were characterized using the following methods: Scanning Electron Microscopy, DTA/TG/MS, X-ray Diffraction method, Raman spectroscopy and Electrochemical Impedance Spectroscopy.

Acknowledgments

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Thermal and spectroscopic study to investigate the effect of the thermal history on the phase behavior of the ionic liquid (C4mim)PF6

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Keywords: Ionic liquid, Polymorphism, Thermal history, Nucleation

Ionic liquid is attractive for application as a green solvent because of the low melting point, negligible vapor pressure, and high thermal stability. Also, it is intriguing from the scientific point of view, because the materials are composed of the steric cation and anion, and has both the Coulombic interaction and the van der Waals force, but it is unclear how these interactions are related to their physical properties. The typical ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, abbreviated as (C_4miim)PF_6, in which the cation has a positive charge on the imidazolium ring and the butyl chain, while the anion has only a negative charge which interacts with the imidazolium ring on the cations. Previously, the thermal study of DSC by Endo et al. showed a polymorphism to clarify three possible crystal forms, α, β, and γ phase, but it is unknown how the order of the stability among the crystals and how each structure arises depending on thermal history. Also, three types of isomers according to the butyl chain of the cations were found by Raman spectroscopy [1], indicating the phase stability is related to the stability of the isomers. However, the X-ray single crystal analysis confirmed that more than two isomers are included for a crystal phase. In this study, we investigate the relationship between the phase stability and the isomerization related to the molecular interaction. The thermal study in which the thermal history was well controlled for (C_4miim)PF_6 by DTA clarify that the γ phase is the most stable forms among the three crystal forms at low temperature and the β phase is more stable than the α phase. However, the IR spectra and DFT calculation indicates that an isomer in the β phase is the most stable among the others. Therefore, it is suggested that the stability of the γ crystal phase is not stemmed from the molecular stability due to the isomerization, but probably the reduction of the enthalpy due to the packing structure. Furthermore, the crystal α form can frequently be found as a first crystal structure by DTA. According to the DFT calculation, the isomer of the cation in the α form strongly interacts with the anion through the hydrogen-bond, while the stability of the isomer itself is the least stable compared with the others expected in the β and γ forms. The hydrogen bond is formed in between the hydrogen on the imidazolium ring of the cation and the fluorine on the anion. The strength of the hydrogen bond was expected with the O-H···F length calculated with the optimized structure by DFT, indicating the Coulombic interaction between the imidazolium cation and anion is dominant in the liquid state and provide the nucleation of the α crystal form in the supercooled liquid state faster than that of the other crystal forms.

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Metals, alloys, intermetallics

Microstructural and thermal response evolution of metallic form-stable phase change materials produced from ball-milled powders

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Keywords: metallic Phase Change Materials, form-stable, thermal stability, Differential Scanning Calorimetry, ball milling

Phase Change Materials (PCMs) are materials in which a phase transition occurs and causes a significant change in at least one material property. When thermal effects are involved, they can be applied in thermal energy management and storage systems, since they can store or release the latent heat associated to the phase transition [1]. Among them, form-stable (FS) PCMs consist of two immiscible phases: a matrix, which provides the structural properties, and an active phase, which undergoes the transition [1].

The PCM characterization involves firstly the analysis of the thermal response. Differential Scanning Calorimetry (DSC) is thus one of the more suitable characterization techniques for Phase Change Materials (PCMs). Phase transformation can be detected through a peak in heat flow signal: it allows to determine the temperature range over which transition occurs as well as the associated enthalpy, i.e. the stored energy. These are far the main properties which characterize PCMs [2]. Moreover, peak shape is also of interest, since it can provide valuable information on the rate (time dependant or temperature dependant) at which thermal energy is stored or released. Considering a FS-PCM, if the phases can be considered homogeneously distributed at the millimetre scales size, then DSC tests performed on small specimen, can be representative of the whole material. This allows to take into account possible interface effects, that could not be considered when only the active phase is tested.

In the design of FS-PCM, leakage of the active phase should be prevented and checked. Further, thermal effect is related to composition, structure and phase amounts: thermal stability, i.e. stability over thermal cycling, of the aforementioned properties is very important for PCM: it can affect thermal efficiency.

This experimental study is focused on metallic FS-PCMs based on an Al-Sn system and obtained by powder metallurgy from ball-milled powders. Particular attention was devoted to shape variation of solidification peaks, which corresponds to energy release, as function of the evolution of alloy microstructure. In order to check thermal stability, DSC tests including several thermal cycles were conducted. Moreover, DSC analyses were performed also before and after several thermal cycles simulating possible operative conditions. Finally, microstructural analysis, through Scanning Electron Microscopy and X-Ray Diffraction, allowed to relate the thermal response variations to microstructural and mechanical changes.

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Investigation of Fe-C-Cr and Fe-C-Cr-Ni based systems with the use of DTA and HT-LSCM methods

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Keywords: DTA, HT-LSCM, temperatures of phase transformations, Fe-C-Cr and Fe-C-Cr-Ni based systems, Thermo-Calc, IDS

The thermophysical and thermodynamic properties of Fe-based systems have been and are still undergoing extensive research. It is necessary to know the behaviour under precisely defined conditions and to have high-quality experimental material data of the most essential simpler systems, such as Fe-C, Fe-C-Cr and Fe-C-Cr-Ni, to predict thermophysical and thermodynamic material properties behaviour of complex systems corresponding to materials used in practice (more complex alloys). Thermophysical and thermodynamic behaviour characterised by material data such as temperatures of phase transformations [1], corresponding latent heats [2], heat capacities [3], enthalpy [4], etc.

All of this key data are important for many SWs such as ProCAST, MAGMASOFT, ANSYS Fluent and similar SW, to simulate manufacturing processes like casting, rolling, forging, welding, heat treatment, to predict diffusion-controlled phase transformations, generally to simulate all processes also involving heat transfer in the material. The material properties are also necessary for the creation of theoretical models for calculations of thermophysical, thermodynamic, kinetic and metallurgical materials properties implemented in many simulation SW based on an empirical and semi-empirical basis, like, e.g. JMatPro, Thermo-Calc, IDS.

Three alloys based on Fe-C-Cr and three alloys based on Fe-C-Cr-Ni were studied. These alloys contained carbon between 0.318 and 0.410 mass%. The content of chromium and nickel was in the range of 0.001 – 4.990 mass%. Temperatures of phase transformations were studied in the high-temperature region. Temperatures of solidus, liquidus and peritectic transformation were detected. The results were experimentally obtained using Differential Thermal Analysis (DTA) and High-Temperature Laser Scanning Confocal Microscopy (HT-LSCM). The Setaram Setsys 18_{TM} was used for experiment with the DTA method. A Laser Scanning Confocal Microscope (VL2000DX from Lasertec) and a high-temperature furnace (SVF17-SP from Yonekura) was used for experiments with HT-LSCM method. All measurements were done by a heating rate of 10°C min-1. Experimental data were compared and discussed with calculation results using SW IDS and Thermo-Calc with use of the TCFE8 (Thermo-Calc Fe-based alloys) database.

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Crystallization kinetics of multicomponent bulk metallic glasses

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The isochronal and isothermal DSC annealing techniques have been employed to investigate the crystallization behavior of multicomponent bulk metallic glasses (BMGs), including two high-entropy BMGs ($Ti_{20}Zr_{20}Cu_{20}Ni_{20}Be_{20}$ and $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$) and a Zr-based BMG with high mixing entropy ($Zr_{40}Hf_{10}Ti_4Y_1Al_{10}Cu_{25}Ni_7Co_2Fe_1$). The continuous DSC curves of the studied multicomponent BMGs show multiple stages of crystallization, indicating that the crystallization process is relatively complex. The activation energies of crystallization were calculated utilizing Kissinger, Ozawa and Boswell models. The crystalline phases corresponding to each crystallization step have been found out. The kinetic fragility of multicomponent BMGs has also been evaluated. Based on the isothermal DSC curves, the Avrami exponent, evaluated from the Hohnson-Mehl-Avrami equation, has been analyzed in detail. It was found that the crystallization process is mainly dominated by growth of particles with a decreasing nucleation rate for HE-BMGs. However, the crystallization behavior of $Zr_{40}Hf_{10}Ti_4Y_1Al_{10}Cu_{25}Ni_7Co_2Fe_1$ BMG exhibits characteristics of both the high entropy BMGs and traditional BMGs with a single principal element. The studied multicomponent BMGs exhibit quite different glass-forming abilities and the related reasons have been discussed.

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Application of thermal analysis in powder metallurgy and additive manufacturing: an overview

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Keywords: surface oxide, sintering atmosphere, reducing agent, alloyed sintered steels, oxide reduction

Metal powder consist a basic feedstock for the number of advanced manufacturing technologies, especially in the group of powder metallurgy and additive manufacturing technologies. Metal powder can be produced by number of methods where gas- and water-atomisation are the dominant industrial manufacturing method. One of the distinctive features of the metal powder is its high surface area, that is about 10 000 times larger than the surface area of the bulk material of the same mass. This, in connection to the small diffusion passes, make this material very reactive.

Typical metal powder is covered by heterogeneous surface oxide, formed by thin (~2 to 8 nm) oxide layer of the base metal, thickness of which is determined by the powder manufacturing method and material reactivity, and covering about 95% of the powder surface. In addition, particulate features formed by thermodynamically stable oxides can be find on the powder surface, sizing up to 100 nm, size and amount of which is also determined by manufacturing method and alloy. Full removal of the base metal oxide layer is required in order to develop strong inter-particle necks. Inability to remove metal oxide layer at low temperatures bring significant risk of the oxide transformation and particulate oxide growth in the areas with poor thermodynamic conditions and high diffusion passes – e.g. growing inter-particle necks in the centre of the component. This brings risk of the weak inter-particle connections and hence low final properties. In case of full powder fusion, presence of the extensive metal oxide significantly affects interaction between the energy source and powder and results in increased effect formation in the final component.

Despite the low thermodynamic stability of the metal oxide in case of steel and Ni-base alloys, oxide removal is very complex process, determined by number of parameters as temperature profile (heating rate, processing/sintering temperature and time), processing atmosphere (composition and purity), compact properties (geometry, density, etc.), powder properties (alloy composition, powder size distribution, surface chemistry, etc.), additives (carbon source, lubricant, etc.), etc. Paper summarised effect of the mentioned above process parameters in correlation to the powder properties based on the kinetics and thermodynamics of the surface oxide transformations. Application of different thermal analysis techniques simulating manufacturing process is described, their advantages and application areas are critically evaluated. Results are related with advanced material characterisation using microscopy and surface analysis techniques as well as thermodynamic simulations.

Adsorption of cadmium on mineral-pseudomonas putida composites at different ratios

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Keywords: Mineral, bacteria, Cd(II), composites, adsorption

Soil is an important sink of various heavy metals. Clay minerals are the main skeleton of soils and microorganisms are the most active living components in soil systems. Clay minerals and bacteria in soils usually form composites or aggregates, which has profound impacts on the species, mobility and fate of heavy metals in soils and associated environments. In this study, we selected three representative clay minerals kaolinite, montmorillonite and goethite, and one bacterial strain *Pseudomonas putida* to study the adsorption of Cd on mineral-bacteria composites at four mineral/bacteria dry weight ratio of 0.1, 0.2, 0.5 and 1.0. The binding characteristics were evaluated through Zeta potential titration, microcalorimetry and batch adsorption experiments. The average particle size of montmorillonite-bacteria composites was larger than those of the other two mineral-bacteria composites. The surface sites of the composites were increased with the proportion of bacteria. The second-order kinetic equation fits the adsorption process well, suggesting the adsorption is chemical adsorption. With the increment of bacterial proportion, the adsorption of Cd(II) on the composites was enhanced. The adsorption affinity and capacity of Cd on the complexes was elevated with increasing proportion of bacteria in the composites. Isothermal titration microcalorimetry experiments indicated that the adsorption of Cd(II) on pure bacteria and 1:1 mineral-bacteria composites were endothermic process, while that on the other three ratio composites were exothermic. Different behaviors of Cd adsorption by the examined mineral-bacteria composites suggest the different binding mechanisms of Cd by soil components and aggregates which is fundamental for the risk assessment and remediation of heavy metal contaminated soils and environments.

Acknowledgments

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Crystallization and oxidation Kinetics of Zr–Cu and zr–hf–cu thin-film metallic glasses

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Keywords: Zr–Cu, Zr–Hf–Cu, metallic glass, crystallization kinetics, oxidation kinetics, activation energy

Recently, binary Zr–Cu and ternary Zr–Hf–Cu thin-film metallic glasses have been prepared and investigated in our laboratories [1,2]. We found that the glass transition and the crystallization temperatures of the Zr–Cu thin films increased gradually with increasing Cu content. A clear correlation between the evolution of the crystallization temperature and mechanical properties with increasing Cu content was observed. In addition, a gradual substitution of Hf for Zr in the films further shifted an onset of the crystallization and the oxidation to higher temperatures.

In this work, we focus on a detailed investigation of the crystallization and oxidation kinetics of $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses and on the comparison of their oxidation kinetics with that of a crystalline $Zr_{54}Cu_{46}$ thin-film alloy. The amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses were prepared by non-reactive magnetron co-sputtering of Zr, Hf and Cu in pure argon. Several as-deposited $Zr_{54}Cu_{46}$ films were post-annealed in high vacuum to create a crystalline thin-film alloy of the identical composition. The non-isothermal crystallization kinetics of the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films was studied by differential scanning calorimetry. The activation energy of the crystallization was obtained by the Kissinger–Akahira–Sunose method. The isothermal oxidation kinetics of the amorphous and crystalline $Zr_{54}Cu_{46}$, and amorphous $Zr_{27}Hf_{27}Cu_{46}$ films was investigated by thermogravimetric analysis. The activation energy of the oxidation was determined by the Arrhenius equation.

The results showed that the $Zr_{54}Cu_{46}$ film crystallized at a lower temperature (≈ 422°C) and in two successive steps in contrast to the $Zr_{27}Hf_{27}Cu_{46}$ film (≈ 477°C). The activation energy of the $Zr_{27}Hf_{27}Cu_{46}$ film was higher for all conversion fractions, which indicates that the substitution of Hf for Zr enhanced the thermal stability of the glassy state. Dynamical thermogravimetric curves revealed that the onset of the oxidation of the amorphous $Zr_{54}Cu_{46}$ film (≈ 475°C) was shifted by about 120°C to a higher temperature than for the crystalline $Zr_{54}Cu_{46}$ film. Moreover, the substitution of Hf for Zr shifted the onset of the oxidation to an even higher temperature (≈ 550°C). As for oxidation kinetics, all isothermal thermogravimetric curves in the temperature range from 400 to 575°C obeyed the parabolic law. The activation energy of the oxidation process was 112, 143 and 208 kJ/mol for the crystalline $Zr_{54}Cu_{46}$ film, and the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films, respectively. The highest activation energy for the $Zr_{27}Hf_{27}Cu_{46}$ film indicates that an oxide layer with the highest protective efficiency was formed on the surface of this film. All these results have been discussed in more detail in our recent paper [3].

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Selection of heat treatment parameters for γ/γ′ W-free Co-based superalloys aided by DTA analysis

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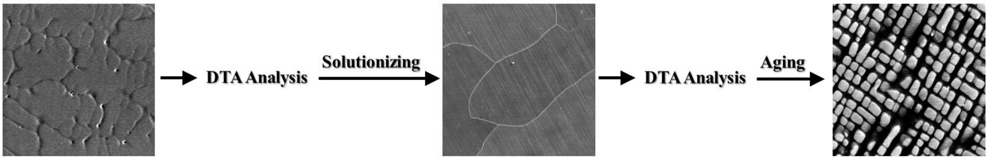
Keywords: γ/γ′, precipitation hardening, superalloys, cobalt, DTA

Recently, the development of novel γ′-hardened Co-based superalloys is related with replacement of W alloying element due to high its high density, which limits the potential of these materials in view of aircraft applications. One group of W-free materials characterized by γ/γ′ structure are alloys based on Co-(Ni)-Al-Mo-Nb/Ta systems [1]. In view of precipitation hardening, the as-cast microstructure of these alloys is unfavourable due to columnar grain structure and numerous eutectic precipitates [2]. Therefore, the obtainment of desirable microstructure requires an appropriate approach assisted by means of thermal analysis (Fig. 1).



As-cast As-solutionized γ/γ′

Fig. 1. Schematic of DTA-aided design of heat treatment of superalloys

The present investigation aims in determination of so called solution heat treatment window and aging parameters for Co-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb (at. %) alloys in order to obtain favourable dual γ/γ′ phase microstructure. For this purpose, the differential thermal analysis (DTA) was utilized as the tool useful in determination of characteristic temperatures connected with microstructural changes. First of all, the DTA analysis was performed for discussed as-cast alloys in the temperature range 40÷1450 °C under Ar protection using NETZSCH STA 449 F3 Jupiter apparatus. The results showed a thermal effect connected with important order-disorder transition and with precipitation/dissolution of undesirable $D0_{19}$ type phases with overall formula Co_3X (where X=Mo,Nb). Moreover, the melting temperature ranges for both alloys were also noticed. Basing on the obtained data, a safe temperature ranges for solution heat treatment was determined (solutioning window). Within such solutionizing window, a temperature range of 1200÷1250 °C was chosen to perform a first heat treatment operation for the investigated alloys. The specimens were annealed at selected temperature for 24 hours. The microstructure of the alloys after solution heat treatment was analyzed as well. Afterwards, the solutionized specimens were subjected to the further thermal analysis in order to select the aging temperature. This parameter can be determined only for the solutionized alloy, characterized by supersaturated solid solution.

This type of DTA analysis was made for both Co-based alloys after solution heat treatment. The DTA analysis revealed that the desirable transformation temperature related with order/disorder process was place at temperature range 900÷950 °C. The order-disorder transformation similar to that of Ni-based superalloys is related to formation of γ′ phase with overall formula $Co_3(Al,X)$ phase, characterized by $L1_2$ type of lattice. All observed transformations were confirmed by SEM/EDS analysis as well as XRD characterization of phase composition of investigated alloys after each stage of the proposed heat treatment.

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Important issues connected with differential thermal analysis of Fe-C based alloys

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Keywords: thermal analysis, DTA, Fe–C based alloys, experimental conditions, decarburisation

The paper deals with issues connected with the investigation of Fe-C based metallic systems by DTA method (generally by thermal analysis methods). There exist many experimental factors that influencing obtained experimental data. Influence of heating/cooling rate [1] must be considered, sample mass also [2], sensors and crucibles used by experiment alone (the whole experimental arrangement), etc. [3]. There are general suggestions how to perform experiments with metallic materials to obtain the desired proper data. But, in many cases it is necessary to modify the experimental conditions substantially with respect to the obtaining of needed data – corresponding data. The problems that can be encountered by investigation of metals with carbon content are also decarburisation and oxidation (often running simultaneously). The paper presents results of experimental measurements performed using DTA method and experimental laboratory system Setaram SETSYS 18TM with respect to the possible decarburisation [4] of studied alloys in low and high temperature region. Fe-C based alloys are investigated in solid and also liquid phase (analysis were performed crossing only solid phase and in addition to that also the melting and solidification process). The degree of decarburisation and its influence on DTA response is discussed. OM and SEM study and change of carbon content of studied samples was performed to determine the possible ratio of decarburisation. The degree of decarburisation can be in some cases considerable [4]. The way how to prevent or minimise the decarburisation degree of Fe-C based alloys during DTA analysis is suggested.

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Performance of AlTi3c0.15 master alloy in refining grain structure of secondary AlSi7Cu3Mg foundry alloys

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Keywords: aluminium alloys, foundry, grain refinement, thermal analysis, microstructure

Grain refinement is a standard practice in Al foundry to guarantee fine and equiaxed grain structure throughout the final component. The Al-Ti-B master alloys are widely used in the Al foundry [1] even if some problems, such as agglomeration of the borides and poisoning by certain elements, are well known; on the contrary, the Al-Ti-C master alloys are less susceptible to these phenomena. The Al-Ti-C grain refiners are widely used for wrought Al alloys [2], otherwise few data are available about the refinement performance of Al-Si based alloys. The purpose of this work is to evaluate the use of thermal analysis to explore the solidification kinetics of secondary AlSi7Cu3Mg alloy after AlTi3C0.15 grain refinement. The on-line prediction of the grain refinement level is very important for quality evaluation and control of alloy castings [3]. Metallographic and thermal analysis techniques, based on two K-type thermocouples' method [4], have been used to quantitatively examine the microstructural changes occurring with AlTi3C0.15 additions. The cooling curves and the corresponding derivative curves have been plotted to determine the nucleation temperature, minimum and growth temperatures for the α-Al reaction. The results indicate how the nucleation temperature progressively moves to higher temperatures by AlTi3C0.15 addition due to an increasing number of nucleation primers (Fig. 1). The lower difference between the maximum recalescence temperature and the maximum undercooling temperature with increasing Ti and C contents indicates the progressive degree of grain refinement. The efficiency of AlTi3C0.15 master alloy seems to decrease with increasing the amount of grain refiner (Fig. 2).

Illustrations

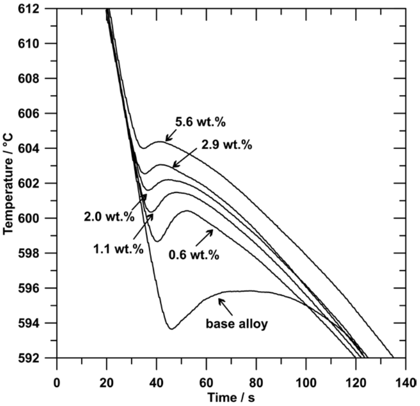

Fig. 1. Cooling curves of the AlSi7Cu3Mg alloy in the region of primary α-Al phase at different AlTi3C0.15 contents (wt.%).

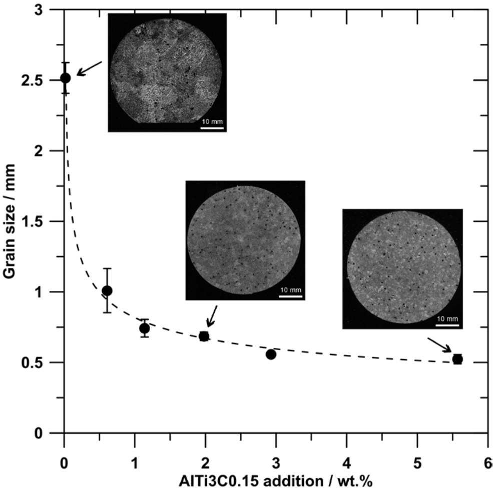

Fig. 2. Average grain size of the AlSi7Cu3Mg alloy as a function of AlTi3C0.15 addition (wt.%).

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Oxide reduction and oxygen removal in water-atomized iron powder – a kinetic study

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Keywords: water-atomized iron powder, thermogravimetric analysis, kinetics, sintering

Water-atomized iron powder is commonly used as the base material in powder metallurgy (PM) for manufacturing of sintered steel. The powder is typically mixed with a lubricant and compacted at large pressures in a die, creating a component of desired shape. This compact is then sintered in order to provide strength to the component. A crucial aspect of sintering is the formation of strong sinter necks between the metal particles. This process is facilitated by removal of the surface iron oxide layer covering all particles, whereby diffusion of metal atoms can proceed to the neck region without hindrance. In addition to the iron oxide layer, the surfaces of the powder particles also contain minor amounts of oxide particulates rich in chromium and manganese, with thermodynamic stability higher than the iron oxide that constitute the surface oxide layer. Inadequate control of the sintering atmosphere and failure to remove the iron oxide layer will not only impede and delay sinter neck formation, but may also cause oxide transformations to occur in which oxygen from easily reduced iron oxides are transferred to elements forming more stable oxides. This effect is believed to deteriorate the mechanical properties of the final state of the sintered component.

In this study, the oxide reduction and oxygen removal in three different size fractions of water-atomized iron powder was investigated by means of thermogravimetric analysis in hydrogen atmospheres. Two principal mass loss events were recorded, corresponding to the removal of the surface iron oxide layer at around 400 °C and a high temperature mass loss event taking place at around 1050 °C. A kinetic analysis was done to determine the activation energies of these mass loss processes. The results yielded activation energies of around 100 kJ/mol and in excess of 400 kJ/mol for the two processes, respectively. The validity of the results were asserted using haematite and magnetite reference samples showing good correlation with the reduction of the surface iron oxide layer. The high temperature mass loss, with no analogy in the reference samples, is believed to be a combination of oxygen removal from thermodynamically stable oxide particulates on the surface as well as internal oxides. Compacts of the water-atomized iron powder, representing the applied setting of industrial importance, were also analysed. Results show a slightly lower activation energy for the first mass loss event which indicates an influence of the compaction step on the initial state of the powder and its oxide layer. The high temperature mass loss event was shifted to higher temperatures, which is believed to be caused by the restricted mass transport of reduction products along the pores in the sintered compact.

Nanofluids

Experimental investigation of ferrofluid flow and heat transfer in a circular tube under constant and alternative magnetic field

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Keywords: Taguchi Method, Ferrofluid stability, Ferrofluid magnetization, Zeta potential, VSM measurement

In this paper, the effect of constant and alternative magnetic field on flow and heat transfer of ferrofluid in a straight tube is experimentally investigated. Fe3O4 nanoparticles in water as a based fluid with two mass fraction of 0.5 and 1 percent are prepared. The effect of different patterns for applying magnetic field is considered. Two constant magnetic field of 770 and 1300 Gauss are study. Alternative magnetic field with different frequency of 10, 100 and 1000 Hertz and different duty cycles are also investigated. Results generally show that using constant magnetic field leads to heat transfer enhancement. Using alternative magnetic field will improve heat transfer till to frequency of 100 Hertz and after that heat transfer is decreased. The tools utilized to characterize and qualify ferrofluids include transmission electron microscopy imaging (TEM), dynamic light scattering (DLS), Zeta potential criteria, vibrating sample magnetometer (VSM), and visual inspection.

Thermal Conductivity Sensitivity of Neutron Irradiated aluminum oxide Nanofluids

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Keywords: neutron irradiation, nanofluids, thermal conductivity, sensitivity analysis, regression analysis, neural networks

Al2O3 nanoparticles have been synthesized using solution combustion method and used for preparation of nanofluids. Prepared nanofluids have been investigated for effect of irradiation on thermophysical properties. Thermal conductivity has been measured for un-irradiated and irradiated nanofluids using KD2 pro thermal properties analyzer. Decrease in thermal conductivity has been observed after neutron irradiation that further decreases with increased duration of exposure and concentration of nanoparticles. 21% decrease in thermal conductivity has been recorded after 14 days of neutron irradiation for 2 volume percent concentration. Soft computing techniques have also been explored as low cost alternative to experimental techniques. Predictive analysis results revealed that though ANN and NuSVR both can be used yet NuSVR exhibited superior performance in terms of computational time and acquired accuracy. Neutron irradiation sensitivity analysis revealed that changes in thermal conductivity are sensitive at higher concentration and during initial exposure of neutron irradiation. The findings point to explore the applicability of nanofluids system to nuclear reactor and conclude the potential application as effective moderator.

Acknowledgments

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Investigation on a novel Hybrid nanofluid for minimum quantity lubrication assisted milling of Inconel 718

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Keywords: hybrid nanofluid, MQL, milling, Inconel 718

Conventional cutting fluids in flood lubrication in metal cutting process improve the machining performance by dissipating the heat generated at the cutting tool and workpiece interface yielding a better tool life, surface finish, and chip removal. However, the bulk uses of the cutting fluids often account for 16-20% of total machining costs, in addition to their handling and management costs. Among existing lubrication techniques, researchers, of late, have focused their attention on minimum quantity lubrication (MQL) which sprays the mixture of compressed air and cutting fluid in an optimized manner instead of flood cooling. The use of nanofluids, owing to their superior thermal and tribological properties, has been recently proposed and shown great opportunities in enhancing the MQL based machining performance. In the present work, a novel glycol based Ag coated ZnO hybrid nanofluid has been proposed for the application in nanofluid based minimum quantity lubrication (NFMQL) assisted machining of difficult-to-cut Inconel 718 superalloy. The proposed nanofluid was synthesized by a two-step method. Initially, the Ag/ZnO hybrid nanoparticles were synthesized by a wet chemical method. Then, as-synthesized nanoparticles dispersed in ethylene glycol at different volume concentrations (ϕ=0.05% to 0.2%). The stability of the nanofluids was observed in terms of zeta potential value and their thermal conductivity was measured by the KD2 Pro instrument. The best nanofluid for NFMQL was selected on the basis of stability and thermal conductivity. The Taguchi L9 orthogonal array was used to design the experimental matrix for various machining settings considering the cutting speed, feed rate, and different coolant conditions viz. dry, flood, and NFMQL. The PVD coated carbide inserts (grade: XOMX0602 F40M) of SECO® were used as cutting tools. The machining performance was analyzed in terms of the average surface roughness and the cutting zone temperature. From the machining experimental results, it was observed that the NFMQL yielded in best machining performance among the considered coolant conditions due to enhanced heat dissipation from cutting zone. Furthermore, the field emission scanning electron microscopic images of used cutting tool inserts reveal that the NFMQL condition induces the less tool wear as compared to other coolant conditions.

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Nanouptake: the European network for nanofluids development related to industrial applications

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Keywords: Nanofluids, Nanouptake, Cost Action, Heating, Cooling, Solar, Boiling, Energy storage, Industrial applications, Conferences

Since the early 1990s, nanofluids received great attention due to their strong potential as heat transfer fluids in energy systems because of their enhanced thermal properties. This interest is part of a wider context of efficient and clean energy demand. Nanofluids science appears as multidisciplinary and far-reaching as many complex phenomena are involved and implies knowledge in many scientific fields, leading to cross-practice collaborations. In this context, almost three years ago, the Nanouptake project [1] was launched by Enrique Julià Bolivar under the auspices of European Cost Association. The main objectives of this scientific project is to create a Europe-wide network of leading R+D+i institutions, and of key industries, to reinforce existing collaborations at European level, to develop and foster the use of nanofluids as advanced heat transfer/thermal storage materials to increase the efficiency of heat exchange and storage systems [1]. With this goal, our European consortium is developing a common understanding of nanofluids preparation and characterization, addressing nanofluids key barriers to the market and creating an open space for new relevant researches.

After a short introduction of the project, we will present its managing organization and the main activities developed by the Action to reach these objectives. Among the activities, and after the first European Conference on Nanofluids in 2017 [2,3] we are organizing the 1st International Conference on Nanofluids (ICNf) coupled to the 2nd European Symposium on Nanofluids (ESNf) by June, 26–28, 2019 in Castellon, Spain [4]. Also, we are creating a database including all type of nanofluids yet studied and experimental equipment's available at European scale. In addition, some examples of common studies and round robin tests [5] performed by Nanouptake participants to increase the knowledge in nanofluids science will be presented.

Such a successful story can encourage researchers and industries to pursue the development of nanofluid research for practical issues in energy and other topics and as well to go further in their research in the field of thermal analysis and calorimetry, energy saving and related materials through joint European programs.

Acknowledgments
PE and LHL acknowledge all members of Nanouptake Cost Action, in particular the Core Group Members and Grant Holder Managers for their strong involvement in the achievement of this joint program. This presentation is dedicated to Enrique Julià Bolivar that was the chair of this Action, nothing would

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Investigation of geometry and nano-fluid propertieis on microchannel performance using Taguchi method and genetic algorithm

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Keywords: Nano fluid, microchannel performance, taguchi method, geentic algorithm

The aim of the present study is to develop and validate a new numerical model to estimate Nusselt number and pressure drop of a nanofluid as a function of ribbed length, the length between each rib, nanoparticle volume fraction, and Reynolds number. For this, the laminar heat transfer of water-Al2O3 nanofluids through a microchannel with quad and triple rib shapes under a constant heat flux was studied numerically by implementing the finite volume method. Simulations were performed using a design of experiments suggested by Taguchi method inside a two-dimensional rectangular microchannel with 4 mm length and 50 µm width. The problem is subjected to maximize and minimize the Nusselt number and pressure loss of the microchannel, respectively. Mathematical models based on the parameters above were developed by using Taguchi method which helps in global optimization using an evolutionary algorithm. The genetic algorithm was utilized to optimize the input parameters and generates the global solution points for the proposed work. In final, at constant Reynolds numbers, the most and least impact on Nusselt number and pressure drop are reported, respectively.

Numerical and experimental study of thermo-magnetic heat transfer by ferrofluids: a review

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Keywords: Ferrofluids, Thermophysical properties, Thermomagnetic convection, Experimental, Numerical, Applications

Ferrofluids or magnetic nanofluids (MNF) are suspensions which constitute a non-magnetic base fluid (generally water) and magnetic nanoparticles. It is a unique class of nanofluids that exhibit both magnetic properties and flow ability similar to any other fluid. In the last decade, ferrofluids has attracted the attention of many researchers for heat transfer and cooling (heat dissipation) applications. Thermal performance of ferrofluids is influenced by the strength of externally applied magnetic field. This novel feature enables to control the thermo-physical and rheological properties, flow of particles and thermo-magnetic convection which make the ferrofluid as promising heat transfer media for industrial applications like in solar thermal systems, photovoltaic systems, industrial heat exchangers, electronic cooling devices, energy harvesters and in micro-channels. This review paper summarizes the recent investigations about most of the commonly-used correlations to predict the effective thermos-physical properties of ferrofluids. Finally, the main aim upon which the present work is based to review on different numerical and experimental approaches to identify the effects of main parameters on thermo-magnetic convection and fluid flow. In addition, this study also comprehensively analysed the applications of ferrofluids, its challenges and potentiality for future research.

A review on nanofluids for heat transfer applications

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Keywords: Heat transfer enhancement; Nanofluids

Fluids play an increasingly important role in our everyday lives including enhanced heat transfer. The development and applications of nanofluids has a significant opportunity for engineers and industry. The approach of thermal properties of conventional fluids to their optimum value does not allow the fulfilment of the present age needs. Therefore, there is an urgent need to develop a new class of fluids tailored as per heat transfer industry requirements. Progress in the past decade has gain momentum in enhancement of heat transfer coefficients of fluids due to development of nano-materials. Recent investigations on nanofluids indicate that the suspended nanoparticles markedly change heat transfer characteristics of the suspension. Nanofluids at low-volume fractions enhance thermal conductivity over base fluid values proving to be a promising material for cooling applications. Thus, they are potentially useful for advanced cooling of thermal systems. This review summarizes concept, recent research on heat transfer characteristics and applications of nanofluids in heat transfer industry as per requirements and identify opportunities for future research. The review tends to be an state of art article giving insights to the reader about nanofluids research including constituents of nanofluids, synthesis of constituents for preparation of nanofluids, approach used for the preparation of nanofluids, applications and potentials of nanofluid research.

Nanomaterials and composites

Synthesis, Characterization of Vanadium Pentoxide Nanoparticles and Determination of Catalase Mimetic Activity by using New Colorimetric Method

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Keywords: Vanadium pentaoxide, V2O5, vanadia, nanoparticles, hydrothermal

Vanadium pentoxide (V_2O_5) nanoparticles, are being widely used in a variety of applications including biological activity studies, construction of solar cells and batteries and in catalyst manufacturing for chemical reactions (e.g.: DENOX REACTIONS). This work introduces a novel colorimetric method used at the first time to determine the catalytic activity (mimetic activity of catalase enzyme) of V_2O_5 nanoparticles by measuring the decrease in color density occurring in the acidic solution of potassium permanganate or V_2O_5 with hydrogen peroxide in room temperature for 3 min at wave length number 525 nm. Vanadium pentoxide was synthesized by hydrothermal method (reflux), from ammonium -metavandate (NH_4VO_3) as precursor, and cetyl- trimethyl- ammonium- bromide (CTAB) dissolved in an ethanol/water mixture solvent as a surfactant solution. The product was annealed at different temperatures (250, 500 and 750 ˚C) for 2 h. The chemical nature and nanostructure of the synthesized nanoparticles were characterized by X-ray diffraction (XRD) which proved that the particle phase is α-V_2O_5. Scanning Electron Microscopy (SEM) was used to study the morphology of the V_2O_5 surface. Atomic Force Microscopy (AFM) was used to determine the imaging surface structures in nm scale to observe the surface roughness. Thermal Gravimetric (TG) investigation has shown the decomposition steps of V_2O_5 at different temperatures. Spectroscopic (UV/Visible) technique was used to record the optical properties of the V_2O_5 nanoparticles and to determine the energy gap of V_2O_5 at different annealing temperature. Fourier Transform Infrared Spectrometer (FTIR) was used to investigate the vibrations of functional groups in vanadium pentoxide. The catalytic activity of these vanandia nanoparticles was studied by using a new colorimetric method against hydrogen peroxide (H_2O_2) as a substrate. The results showed that the catalytic activity of vanadium pentoxide nanoparticles increases directly with the annealing temperature to reach the maximum activity after annealing at 500 ˚C and after that it decreases with increasing annealing temperature.

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Graphene filled polymer composites with enhanced thermal properties

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Keywords: graphene, polymer, composite, processing, thermal properties

Due to the astonishing high value of thermal conductivity (TC) of experimentally around 5300 $Wm^{-1}K^{-1}$ graphene is paid great attention for possible application in heat management of electronic devices. Tremendous investigations have been recently conducted to increase the TC of nanofiller filled thermoplastic composites. However, the agglomeration of nanofillers limits the loading of graphene and has been a bottleneck to further increase TC of polymer composites. Therefore, the key technique to solve this problem is to invent new method to get homogeneously dispersed graphene filled polymer composites. In this work, a preparation technique combining the benefits of both solution mixing and melt blending is proposed. With this technique, the loading of graphene can be as high as 20 wt% and simultaneously good dispersion of graphene sheets is achieved in the polyamide 6 (PA6) matrix. The TC of the composites reaches 3.55 $W\ m^{-1}K^{-1}$, corresponding to a TC enhancement of 1167% compared to pure PA6. The excellent performance of composites can be attributed to high filler loading, uniform dispersion of graphene sheets, as well as high crystallinity of the matrix. Above factors facilitate the formation of continuous conductive network inside the composites which increases the efficiency of heat transfer. Besides, as-obtained composites show much better mechanical properties compared to pure PA6, which reflects the reinforcement effect of graphene sheets on polymer. The results obtained in this work provide an effective and facile route for developing low-cost and high TC thermoplastic composites, as well as open new possibility to engineering application of such composites.

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Influence of graphene oxide composition on photocatalytic properties

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Keywords: graphene oxide, TG/DTA-MS, photocatalysis

Graphene oxide (GO) is a widely investigated nanostructured carbon-based material in a number of research areas, such as gas sensing and photocatalysis. It can be easily prepared by liquid phase exfoliation of graphite, and by subsequent reduction of the GO. The graphene structure can be restored to get reduced GO (RGO), by heat treatment or chemical reduction. GO can be a good support material for photocatalysts, because of its high specific surface area and capability of being an electron acceptor, and even shows photocatalytic activity by itself. In this study, we prepared graphene oxide with the improved Hummers' method. We investigated the thermal behaviour of GO in oxidizing (air), inert (N_2) and reducing (5% H_2/95% Ar) atmospheres in detail by TG/DTA-MS. Based on the results, GO was annealed in the different atmospheres at 200 and 300 °C to prepare GO samples with different functional group and heteroatom content. The morphology and composition of the samples were examined with Raman and ATR-FTIR spectroscopy, SEM-EDX, TEM and XRD. Photocatalytic activity was investigated in decomposing methyl orange dye with the aim to see how the different chemical properties of GO samples influence the photocatalytic performance.

Investigation of synthesis dynamics of graphite oxide

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Keywords: synthesis, graphite oxide, thermal analysis, Hummers method

Synthesis dynamics of graphite oxide were studied using a sampling technique. The synthesis of graphite oxide was carried out by the modified Hummers' method [1]. The possibility to obtain the different types of graphite oxides by this method was shown [2]. Small samples of the solid phase (10–50 mg) were collected from the reaction mixture and analyzed using thermogravimetric analysis (TG), differential scanning calorimetry (DSC), scanning electron microscopy, X-ray diffraction, Raman spectroscopy, energy dissipative X-ray spectroscopy, and X-ray photoelectron spectroscopy (XPS). The formation of the intercalated phase of graphite oxide at 60 min from the start of the synthesis (20 min after the addition KMnO4) was confirmed by TG/DSC and XPS. XPS confirms that the addition of H2O2 plays a significant role, not only in the removal of impurities but also in the increase in the GO oxidation degree that is reflected by the higher concentration of C–O, C=O, and COOH groups. Differential scanning calorimetry and thermogravimetric analysis data confirmed that the addition of ice and H2O2 induce the stronger formation of surface functional groups instead of intercalated guest species and it leads to an increase in the concentration of the COOH group, whereas the concentration of C=O groups only changes slightly.

Acknowledgments

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Rheology and its temperature-dependence in thermosensitive copolymer-clay systems

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Keywords: clay nanoparticles, triblock copolymer, rheology, calorimetry, structure

Polymer-clay nanoparticles systems are attracting a large interest primarily because property enhancements could be achieved at either very low polymer or nanoparticle volume fractions. However, the understanding of the rheology and structure of these materials, particularly in the intermediate concentration regime, is still challenging. The purpose of this presentation is to provide an insight into the role of each component in influencing the fluid-solid transition induced by temperature.

The system consists of a thermosensitive copolymer micellar solution, a pluronic triblock copolymer in solution to which we add synthetic clay laponite nanoparticles. The concentrated micellar solutions exhibit a temperature induced phase transition from fluid to crystal. Addition of clay nanoparticles is found to promote the formation of polycrystallized micellar micrograins, above the transition temperature, instead of a cubic monocrystal. This polycrystallization is associated with the confinement of the nanoparticles, which play the role of impurities, in interstices between the micrograins.

We will describe the thermo-rheological proprieties of the nanocomposites in the relatively concentrated nanoparticle range. The viscoelastic behavior, and its temperature-dependence, will be discussed. These results will also be discussed in the light of additional information obtained from structural studies performed on these systems.

Cooling curve thermal analysis of ex-situ A356-YSZ metal matrix composite

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Keywords: Metal matrix composite, YSZ, A356, thermal analysis, solid fraction

This research emphasises the characteristic features of an Al-Si/YSZ ex-situ composite, with the addition of bismuth, employing computer-aided cooling curve thermal analysis (CA-CCTA). The results show that the addition of YSZ particles induces a decrease in solidification time in compare to A356 matrix alloy. It can be seen that the liquidus temperature or nucleation temperature of Al dendrite decreased from 621.4°C to 616°C with addition of YSZ reinforcement. Besides, addition of YSZ did not show substantial effect on the formation of eutectic Al-Si. Eutectic growth temperature (T_G) was measured at 568.4°C and 568.5°C for A356 alloy and A356+YSZ composite respectively. However, addition of Bi cause to decrease of eutectic growth temperature (TG) down to 566.9 °C. Solidification rate which is defined as $\Delta T/\Delta t$ was 0.11 °C/s for matrix alloy which is increased to 0.14°C/s after addition of YSZ particles.

Exfoliation, surface modification and photocatalytic application of an iron-rich kaolinite

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Clay minerals as abundant, cheap raw materials are potential candidates for use in environmental remediation technologies. Due to their high adsorption capacity these materials can efficiently be used for immobilization of different environmental pollutants. The 2:1 type minerals (e.g. montmorillonites) can be expanded with long-chain alkylamine cations to produce adsorbents for the removal of phenolic compounds from water [1].

The discovery of the photochemical activity of exfoliated kaolinites opened new horizons in the mineralization of organic pollutants in water upon UV irradiation [2]. It has been shown that the separation of the TO layers is essential for the photochemical activity, but the contribution of structural defects and mineral pollutants to the catalytic effect is still unclear. The main goal of our work is the systematic study of the factors that influence photodegradation.

The present study describes the exfoliation and photochemical properties of an iron-rich (7% w/w Fe_2O_3), highly-ordered kaolin with and without the presence of iron-pollutants. Exfoliation was achieved with a four-step displacement intercalation method, using potassium-acetate, ethylene-glycol, hexylamine and toluene as reagents. After the last step, the surface was cleaned with acetone, isopropyl-alcohol and MilliQ-water to remove adsorbed organic reagents from the surface. Structural changes occurred during intercalation were followed by means of X-ray diffraction (XRD), thermal analysis (TG/DTG) and infrared spectroscopy (FTIR-ATR). The morphological changes were examined with nitrogen adsorption experiments and scanning electron microscopy (SEM). Surprisingly, the removal of the organic contaminants from the surface resulted in a partially reordered structure. Also, the formation of the typical nanoscroll structure after exfoliation was hindered, possibly due to the existence of structural iron. The photodegradation activity was studied by the 365 nm UV irradiation-induced decomposition of surface-adsorbed model compounds (sodium-benzenesulfonate in the solid and oxalic acid in the liquid phase). In addition, the mineralization efficiency of the raw kaolin, the exfoliated nanostructure, as well as the acid-treated and silver-coated derivatives were also investigated. The highest photochemical activity was observed in the case of the acid-treated samples.

Acknowledgement

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Impact of BTiO3 nanoparticles of different particle sizes on phase transitions in smectic A liquid crystal

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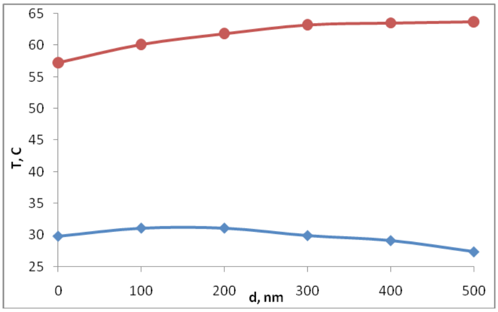
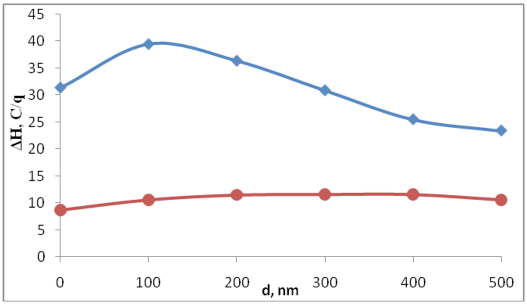
In the work, the influence of BaTiO3 particles on the phase transitions of smectic A liquid cyrstal was studied. It was shown that, BaTiO3 particles increases the temperature of smectic A to izotrop phase transitions. This increase becomes larger with the growing of the size of particles. This increase is about 5.5 oC in case of 500 nm size BaTiO3 particles.



BaTiO3 particles increases the entalpy of smectic A - izotrop phase transition. In average sizes (200–400 nm), this increase becomes even larger. The temperature of crystal to smectic A phase transition rises for small sizes of BaTiO3 particles (200 nm, 400 nm), but it drops for large sizes (300–500 nm). The same is valid for the enthalpy of the crystal to smectic A phase transition.



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The effect of cross-linking agent and initiator on the thermal conductivity and cure kinetics of epoxy-boron nitride composites

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Keywords: epoxy, thiol, boron nitride, diamine, thermal conductivity, differential scanning calorimetry (DSC)

There are many parameters which affect the thermal conductivity of composites of epoxy and boron nitride (BN), including BN content, BN particle size and shape (platelets or agglomerates), cross-linking system, and whether or not the BN particles are surface treated [1]. In earlier work [2], we investigated the effect of BN platelet size in an epoxy-thiol composite, and showed that the thermal conductivity increased as the BN platelet size increased, and that this was accompanied by a systematic variation in the cure kinetics. In the present work we investigate the influence of (i) different cross-linking agents, and (ii) different initiators, on the thermal conductivity and cure kinetics of composites filled with 30 μm BN platelets up to 45 vol%.

For the first study, we compare an epoxy-thiol system, initiated with a latent encapsulated imidazole (LC-80), and denoted ETLBN30, with an epoxy-diamine (Jeffamine) system, denoted EJBN30. The effect of BN content on the cure reaction kinetics has been studied by differential scanning calorimetry (DSC) and the thermal conductivity of the cured samples has been measured by the Transient Hot Bridge method. The heat of reaction and the glass transition temperature of the fully cured samples are independent of the BN content for both cross-linking systems, indicating that the network structure is independent of the BN content. On the other hand, the peak exotherm temperature or time, in non-isothermal and isothermal cure, respectively, for the epoxy-thiol system both increase with filler content, whereas they remain essentially constant for the EJBN30 system. This dependence of the cure kinetics on BN content for the epoxy-thiol system is attributed to a Lewis acid-base interaction [3] between the thiol and the BN particles, and is reflected in an increased thermal conductivity for the epoxy-thiol system for the same BN content, as a consequence of the improved interface between the BN particles and epoxy matrix. For both systems, the thermal conductivity increases with BN content, but for ETLBN30, which is cross-linked with the thiol, it reaches the higher value of 3.34 W/mK for 45 vol% in comparison with 2.37 W/mK for the epoxy-diamine system, EJBN30, again indicating a better matrix-filler interface for the epoxy-thiol system.

For the second study, we investigate the effect of using an alternative initiator, N,N-dimethyl-N-phenyl urea (Technicure, PDU-250M), giving a composite system denoted ETPBN30. For the system ETPBN30, the peak exotherm temperature increases with BN content in non-isothermal cure, and the time to the peak exotherm in isothermal cure also increases with BN content, in the same way as for the ETLBN30 system. This dependence on BN content is consistent with the association of this effect with the presence of the thiol, but the temperature range for curing is significantly higher for ETPBN30 than it is for ETLBN30. For the ETPBN30 system, the thermal conductivity again shows a systematic increase with increasing BN content, and there is no significant difference between the thermal conductivities of the ETLBN30 and ETPBN30 systems, both being significantly higher than those for the epoxy-diamine system.

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Janus superhydrophilic/superhydrophobic nanofiber membrane decorated with CNT for oil water separation

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Keywords: oil-water separation, janus membrane, electrospun nanofiber, superhydrophobic, super hydrophilic

With a rampant discharge of oily wastewater from industrial and domestic sources, as well as the frequent oil spills embarked a severe environmental impact. With the goal to address this dilemma, oil water separation technology has attracted great attention. One of these resolutions is oil water separation with janus surface properties that can be conveyed on both water in oil and oil in water emulsions. With the aim to design a facile oil water phase separation a nanofiber decorated with CNT were fabricated by electrospinning nanofiber membrane for the superhydrophobic side and subsequent interfacial polymerization of Polyamide on the superhydrophilic side of the membrane. The janus nanofiber membrane architecture were designed by taking advantage on the hydrophilic property of polyvinyl alcohol and hydrophobic property of CNT. The designed decorated nanofiber is scrutinized in different oil water emulsion conditions to test its asymmetric wettability properties to demonstrate the switchable oil water parting performance and efficiency.

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Study of thermal and mechanical properties of crosslinked polyethylene/expanded graphene nanocomposites

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Keywords: crosslinked polyethylene, expanded graphene, nanocomposites, thermal analysis

The pipe industry has focused on polyethylene pipes for geothermal heating and cooling systems. The need for polyethylene materials with improved thermal stability has led to the development of crosslinked polyethylene (PEX), which possesses has increased molecular weight, high elastic modulus and impact resistance [1]. However, the main disadvantage of PEX is the low thermal conductivity which limits its application. Therefore, in this work, PEX/Expanded Graphene (EG) nanocomposites were prepared by the melt mixing method. Prior to PEX/EG preparation, expanded graphite was exfoliated using heat treatment and after that, it was dispersed in High Density Polyethylene (HDPE) matrix via melt compounding in order to improve the dispersion of graphene in the final PEX nanocomposites. The effect of various loadings of HDPE/EG on the thermal and mechanical properties of the PEX/EG nanocomposites was studied. The thermal stability of PEX and its corresponding nanocomposites was studied by using Thermogravimetric Analysis (TGA). The degree of polymers' crystallinity was also calculated by Differential Scanning Calorimetry (DSC). The thermal conductivity of the samples was measured by a new device, based on the hot/cold tank principle [2]. Finally, the mechanical properties testings were performed to determine the values of Young's modulus, tensile strength at yield, tensile strength at break and elongation at break. PEX/EG nanocomposites were found to present increased thermal stability and conductivity compared to neat PEX.

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Thermal properties of TiO_2 nanofibers synthesized by electrospinning using water soluble Ti-precursor

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Keywords: TiBALDH, PVP, Electrospinning, Annealing, TiO_2, TG/DTA-MS, FTIR, XRD and SEM-EDX

A new electrospinning process was developed for preparing TiO_2 nanofibers using a water soluble Ti-precursor, titanium (IV) bis(ammonium lactato)dihydroxide (TiBALDH). The importance of the study is justified by the fact that Ti-precursors used for electrospinning, sol-gel, hydrothermal and other fiber synthesis processes are mostly non-water soluble. Accordingly, anatase TiO_2 nanofibers of diameter between 20–140 nm were synthesized by electrospinning and annealing. Polyvinylpyrrolidone (PVP) and different concentrations of TiBALDH were dissolved in a mixture of water, ethyl alcohol and acetic acid to optimize the electrospinning conditions. The as-spun fibers were studied using TG/DTA-MS to establish annealing conditions. The fibers were then annealed at 1 ºC min^{-1} until 600 ºC to get TiO_2 nanofibers. The nanofibers were characterized using FTIR, XRD and SEM-EDX. The photocatalytic property of the fibers was studied.

Modification of nanocrystalline cellulose toward fabrication of bio-based polyamide composites

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Keywords: cellulose, modification, thermal properties

Cellulose nanocrystals (CNCs) are getting an increased attention as bio-based fillers with excellent mechanical characteristics that are applied in polymer composites and hybrid materials. CNCs are considered as functional nanofillers able to improve various properties of polymer composite materials, such as thermal, mechanical and barrier properties. Preparation routes of cellulose nanocrystals include those based on hydrolysis of cellulose materials in mineral acids; however, cellulose nanocrystals commonly obtained from sulphuric acid are characterized by relatively low thermal stability [1]. Recent studies revealed that the use of phosphoric acid leads to CNCs characterized by higher thermal stability [2,3] which is an important parameter during the processing of polymer composites by e.g. extrusion method. Hydrolysis process of cellulose materials depends on the kind of substrate, reaction conditions and purification procedures, so elaboration of a standardized procedure could essentially help to produce CNCs with improved properties.

An important issue is surface functionalization of CNCs to increase the compatibility with polymer matrices; this process can be performed through e.g. esterification, etherification or grafting [4]. In our work we have applied succinic anhydride for surface modification of CNCs and investigated the influence of reaction conditions on the structure and thermal properties of modified cellulose nanocrystals. They can be utilised as reinforcing agents for biopolymers produced from renewable raw materials that are an environmentally friendly alternative to conventional petroleum-based polymers. Among bio-based polymers bio-polyamides (bio-PAs) are a class of engineering polymers with excellent mechanical, barrier and thermal properties. Importantly, they are also characterised by good processability by e.g. extrusion and injection moulding methods which is advantageous for future industrial applications.

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Probing the multifunctional behaviour of Barium zirconate/barium titanate/epoxy resin hybrid nanodielectrics

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Keywords: ferroelectrics, dielectric relaxation, energy storage, multifunctionality

As nanodielectrics are referred the following categories of materials: (a) polycrystalline semiconducting or insulating materials, with grain diameter at the nanoscale level and (b) polymer composites incorporating nanoinclusions. Ceramic/polymer composite nanodielectrics exhibit tunable thermal, mechanical, electrical and magnetic properties, energy storing ability and at the same time processabilty and resistance to corrosive environments. Thus, their performance is characterized by multifunctionality since structural components are able to perform a wide range of desirable functions. By employing filler nanoparticles such as polar oxides and/or piezo/ferro-electrics, or any kind of stimulus responsive materials additional functional performance is induced in the nanocomposites, which can be exploited as a suitable basis for the development of smart materials [1-5].

In this study, hybrid composite nanodielectrics of epoxy resin and $BaZrO_3$/$BaTiO_3$ ceramic nanoparticles were prepared via a mixing process varying filler content. Composites' morphology was studied via scanning electron microscopy (SEM) and in all cases fine nanodispersions were detected. The electrical response of the employed nanofilers, as well as of the produced hybrid composite specimens, was examined by means of broadband dielectric spectroscopy (BDS) in a wide temperature and frequency range. The thermally varying polarization of the embedded nanoparticles induces functionality to the composite systems, due to the thermally triggered structural transitions of $BaZrO_3$ and $BaTiO_3$. Aiming to investigate these structural transitions samples were studied by means of several experimental techniques including x-ray diffraction (XRD), laser Raman spectroscopy (LRS) and differential scanning calorimetry (DSC) with temperature as a parameter.

Dielectric results denoted the presence of three relaxation processes, namely glass to rubber transition of the polymer matrix, re-arrangement of polar side groups of the macromolecules and interfacial polarization. Dielectric data analyzed via the dielectric reinforcing function provided evidence for the ferroelectric to paraelectric transition of barium titanate approximately at 140ºC and for the ferroelectric and/or anti-ferroelectric behaviour of barium zirconate approximately at 40ºC, being in accordance with the results from the analytical techniques. The real part of dielectric permittivity increases with filler content, although optimum performance does not correspond always to the maximum reinforcing phase content.

Finally, the ability of the examined nanosystems to store and harvest energy under various conditions was examined and discussed in tandem with the mutual interactions of the occurring physical mechanisms at specific temperature ranges.

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High thermal conductive epoxy resin composite with titanium oxide nanoparticle modified by stearic acid and benzoic acid in supercritical carbon dioxide

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Supercritical carbon dioxide ($scCO_2$) is expected as an alternative green solvent in place of organic compounds and surfactants, which were used so far in the reaction media for the conventional modification process. We examined the surface modification of nano-sized composites with several kinds of functional compounds in $scCO_2$. We could produce the titanium oxide (TiO_2) composites modified with stearic acid and benzoic acid being capable of dissolving stably into organic solvents previously [1,2]. TiO_2 nanoparticles modified with stearic acid and benzoic acid as a hydrophobic dispersant were synthesized in $scCO_2$ over the temperature and the pressure ranges. The amount of stearic acid and benzoic acid modified on the surface of TiO_2 was determined by the thermogravimetric analysis. The amount of stearic acid and benzoic acid immobilized on the surface of TiO_2 increased with the reaction temperature and the density of $scCO_2$. This can be explained by $scCO_2$ solubility dissolved into molten stearic acid and benzoic acid and reaction kinetics between hydroxyl group on the surface of TiO_2 and carboxylic group of stearic acid and benzoic acid. However the amount of stearic acid and benzoic acid modified on the surface of TiO_2 was reduced from the pressure ranges of 15 MPa to 20 MPa. The surface morphology of synthesized TiO_2 composites was observed by scanning electron microscopy. FT-IR spectra obtained from the composite molecule show that the hydroxyl group on the surface of TiO_2 was chemically grafted by the carboxylic group of stearic acid and benzoic acid. Furthermore, we develop higher thermal conductive epoxy resin with the TiO_2 composites modified by stearic acid and benzoic acid for thermal management of electronic devices. The thermal conductivity of epoxy resin with the TiO_2 composites modified by stearic acid and benzoic acid dispersed in epoxy resin was measured. We found that the thermal conductivity of the epoxy resin with the benzoic acid modification nanocomposite was up to three times higher than those of conventional epoxy resin.

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Review on modeling of mechanical properties and thermal conductivity of graphene nanoplatelets reinoforced high-density polyethylene composites

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Keywords: HDPE, Graphene, mechanical properties, thermal conductivity, modeling

Recently, there has been a growing interest toward nanocomposites applied in thermally conductive polymeric materials. Carbon-based nanomaterials, such as carbon black, carbon nanotubes and high aspect ratio graphene nanoplatelets (GNPs) have been proposed to be the next generation of multifunctional nanofillers for the improvement of thermal and mechanical properties of polymer matrices [1]. GNPs are ultrathin particles of graphite that can be thought of as short stacks of graphene sheets. The addition of GNPs to the polymer matrix allows a superior enhancement of the thermal and mechanical properties at a very low filler loading because of high intrinsic thermal conductivity, large specific surface area, and high two-dimensional sheet geometry [2]. In this work, a series of GNPs- reinforced thermoplastic high-density polyethylene (HDPE) were prepared by the melt-mixing method, with the introduction of GNPs of different diameter (5, 15 and 25 μm in diameter, 6 to 8 nm in average thickness) at various filler contents (from 0.5 to 5 wt.%). The solid-state structure of HDPE nanocomposites was then investigated by X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Polarized Light Microscopy (PLM), and Transmission Electron Microscopy (TEM). Thermal diffusivity measurements were taken using the Laser Flash Analysis (LFA). The effectiveness of selected micromechanical models on predicting the nanocomposites' thermal conductivity was examined too. Mechanical properties testing was performed on an Instron 3344 dynamometer, in accordance with ASTM D638. Various micromechanical models such as Voigt, Reuss, Halpin-Tsai, Takayanagi, etc. were tested in order to compare their predictions with the experimental data and evaluate the elastic behaviour of the prepared composites. Finally, Scanning Electron Microscopy (SEM) was used to analyze the strengthening mechanism of the HDPE/GNPs nanocomposites. Buckling of the sheets occurs at their edges, giving rise to intense contrast of the (0002) planes of graphene. An inhomogeneous distribution of GNP agglomerates within the matrix was found. As the diameter size and filler content increase, the agglomeration becomes reductive to the nucleation activity of nanocomposites and supportive to the development of larger aggregates. However, larger aggregate particles result in a greater contact area increasing the path for phonon diffusion within nanofillers and thus improving the thermal properties of the HDPE matrix. So, HDPE/GNPs nanocomposites show higher thermal conductivity values compared to neat HDPE, while the experimental data are in agreement with the Hatta–Taya theoretical model. GNPs also improve the mechanical properties of HDPE matrix, manifested by the increase of Young modulus and tensile strength. The Halpin-Tsai equation gives a reasonable estimate for the effective stiffness in HDPE/GNPs nanocomposites, but the modified Takayanagi model is considered more accurate for high aspect ratio fillers. SEM image of reinforced composites shows the strong interface between the GNPs and the HDPE, which is an indication that tensile load is effectively transferred from the matrix to the GNPs. However, agglomeration occurs at high filler's concentration due to the Van der Waals force of the nanoplatelets which are slipped during the tensile testing causing the decrease of impact properties of the composites. Summing up the influence of filler's size on thermal and mechanical properties of the polymer matrix, GNPs with the higher diameter size affect more than the smaller ones.

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Effect of size, shape and dimension on glass transition and Kauzmann temperature of Ag and Ta nanoparticles

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Keywords: Glass transition temperature, Kauzmann temperature, nanoparticles

In the field of nanotechnology, size plays a vital role to modify the physical, mechanical and chemical properties. Thus has resulted a wide application of nanoparticles into various fields. The liquid–glass transition phenomenon is observed in various types of liquids, including molecular, ionic, metallic, oxide, and chalcogenide liquids. For example, vitrification of monoatomic metallic liquids is extremely difficult. However, Zhong *et al.* achieved an unprecedentedly high quenching rate of 10^{14} K/s in nanoscale and first in experiment vitrified the monoatomic metallic liquids on the extremely small nano-tips[1]. Futher glass transition temperature T_g and the corresponding Kauzmann temperature T_K, are often used to characterize vitrification of a supercooled liquid. Further Computer simulation is been used to show that $T_K(D)$ of selected size will be smaller than the bulk T_K [2]. Because of kinetic restrictions it is difficult to measure direct experimental data for T_K. But it can be indirectly determined by extrapolation from experimental data based on some theoretical models, such as the Vogel–Fulcher law with viscosity measurements for estimation of Kauzmann temperature. A simple model is developed to calculate size, shape and dimension dependent Glass transition (T_g) and Kauzmann temperature (T_k) of Ag and Ta nanoparticles(NPs) using cohesive energy model. In this study we have selected Ag and Ta nanoparticles (NPs) with spherical, tetrahedral, octahedral and icosahedral shapes accompanied with 0-, 1- and 2-dimensions. In terms of size, both nanoparticles decreases with decrease in size at nanoscale irrespective of shape and dimension. In terms of shape; it is observed that T_g,T_K (icosahedral,D) > T_g,T_K (spherical,D) > T_g,T_K (octahedral,D) > T_g ,T_K (tetrahedral,D) for selected nanoparticle. In terms of dimension; T_g, T_K (d=0) < T_g, T_K (d=1) < T_g, T_K (d=2) for selected size and metallic nanoparticle. However distinguished feature in terms of Glass transition and Kauzmann temperature with respect to size, shape and dimension can be observed only within nanoscale. The calculated values of T_g and T_K for Ag and Ta naoparticles are compared and found consistent with the available MD simulation data [2,3].

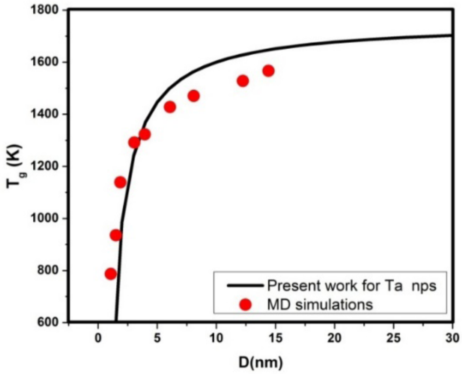

Fig.1 T_K(D)function of Ag as a function of size (D)

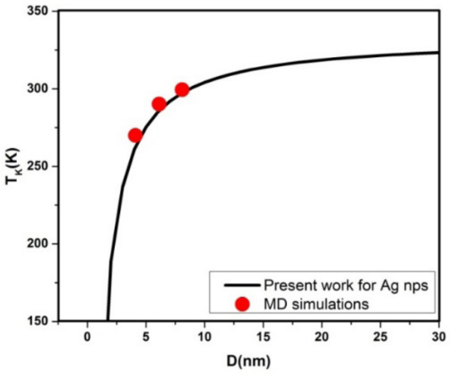

Fig.1 T_g(D)function of Ta as a function of size (D) .

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Influence of the modified iron content on the photocatalytic activity of kaolinite

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Keywords: kaolinite, iron-content, photocatalytic activity, controlled rate thermal analysis

Application of clay minerals depends on their surface and structural properties such as crystal structure, structural and mineral impurities, morphology and porosity. The recently discovered photocatalytic activity of kaolinite-type clay minerals enables their use as (co)catalyst [1, 2].

The present study describes the investigation of an iron-rich kaolin. It was found that the concentration and the structural form of iron (lattice or mineral impurities) can strongly influence (photo) catalytic activity.

Selective acidic treatment (with hydrochloric and sulfuric acids) of the raw kaolin was carried out to determine the available iron content. Using hydrochloric acid of different concentrations and contact time, it is possible to control residual iron in the structure and on the surface. However, the pore structure is also changed with the treatment.

To characterize the modified kaolin the following methods were used:

- Thermal analysis: observation of the effect of acidic treatment on the mineral composition and structural OH groups. In order to resolve the closely overlapping decomposition steps controlled-rate thermal analysis was applied;
- 27Al MAS NMR spectroscopy: investigation of coordination state of Al atoms;
- Specific surface area measurements: BET/BJH surface area, and pore size distribution;
- XRD: observation of mineral impurities (hematite, goethite) and changes in the structural order;
- ICP-OES: determination of leached and residual iron and aluminum;
- TEM: imaging the morphological changes during treatments.

The samples were tested for their photocatalytic activity. A 365nm UV radiation was applied to decompose the test molecule oxalic acid. The mineralization process was followed in solution via permanganometry. The effect of pH on the rate of decomposition was also inv estigated.

Information resulted from the above investigation is important in the development of photocatalysts with tailored surface properties.

Acknowledgements

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Synthesis, characterisation and photocatalytic application of halloysite-based nano-hybrids

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Keywords: nano-halloysite, TiO_2 hybrids, thermal synthesis, photocatalytic activity

Novel environmental remediation technologies increasingly require efficient, cheap and environment-friendly catalysts. The abundant, natural clay minerals are good alternatives as adsorbents, catalyst supports or co-catalysts. Their application depends mainly on their surface properties, which could be extended by surface modification. The catalytic activity of clays is related to the properties of octahedral alumina sheet and its defect sites.

Halloysite is a 1:1 type, layered phylloaluminosilicate, constituted by Si^{4+}-centered tetrahedral (T) and Al^{3+}-centered octahedral (O) layers. The 1:1 type phylloaluminosilicates are shown to be potential photocatalysts, while exfoliation increases the photochemical activity [1-2]. Titanium-dioxide is a well-know and widely used semiconductor-type photocatalyst, which can enhance the photocatalytic efficiency of clays via surface deposition.

This present study describes the characterization and photochemical application of halloysite-TiO_2 hybrids, synthesized from a commercially available halloysite nanoclay. Nanohalloysite-TiO_2 hybrids were synthesized via sol-gel preparation and controlled thermal oxidation in dynamic air atmosphere. The dehydration and dehydroxylation of untreated nanohalloysite were studied by thermoanalytical methods (TG, DTG, DTA). Thermal analysis was used to determine the optimum temperature and isothermal parameters of the halloysite-titanium-gel oxidation, without detrimental structural alternation of the nanohalloysite. Vibrational spectroscopy (FTIR-ATR, Raman micro-spectroscopy) and X-ray diffraction (XRD) were used to investigate structural changes after heat treatment. Fourier-transform infrared spectroscopy indicates no major structural damage of the halloysite TO layers. The surface-deposited TiO_2 was identified as anatase by Raman micro-spectroscopy, which was confirmed by XRD and electron diffraction, as well. Morphological examinations by transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) mappings indicate 15-20 nm-sized TiO_2 crystallites on the surface of the halloysite nanoscrolls. Pore volume distribution and specific surface area (BET/BJH-SSA) were characterized by nitrogen adsorption. The band gap values of the hybrids were surprisingly lower than that of the commercially available Degussa P25 TiO_2, as revealed by UV-Vis-DRIFT measurements. The photocatalytic activity of the untreated nanohalloysite and the nanohalloysite-TiO_2 hybrids was studied by the decomposition of oxalic acid test compound in aqueous phase upon 365nm UV irradiation. The results were compared to the photocatalytic efficiency of commercially available Degussa P25 TiO_2 and pure synthetic TiO_2, used as references. The untreated nanohalloysite showed a moderate catalytic efficiency which was improved by surface TiO_2 deposition.

Acknowledgments

This research was financially supported by the European Union, co-financed by the Széchenyi 2020 program under grants No. GINOP-2.3.2-15-2016-00016 and GINOP-2.3.2-15-2016-00053.

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Pharmaceuticals

Thermal behavior of anti-inflammatory drug naproxen

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Keywords: Naproxen, Thermal decomposition, Evolved gases analysis

Naproxen (NAP) ((+)-(S)-2-(6-methoxynaphthalen-2-yl) propionic acid) is non-steroidal anti-inflammatory (AINES) drug, that presents anti-inflammatory, anti-thermic and analgesic action related to the inhibition of cyclooxygenase enzymes COX1 and COX2. These enzymes catalyze the production of prostaglandines, which are lipids physiologically active that induce the inflammation process.[1] The combination of thermal analysis with complementary spectroscopic techniques permits detailed investigation on thermal behavior of several materials including drugs. Such studies involves thermal decomposition, thermal stability, reactions in solid state, purity of drugs, physical transformations, polymorphic transitions, melting point, crystallization, evolution of gases, among others changes.[2-5] Some previous reports about thermal analysis of naproxen can be found, however, none of them proposed a thermal decomposition mechanism to this drug.[6-11] Therefore, in this report thermal analysis techniques, TG/DTG/DTA, DSC and TG-FTIR, were used to detailed investigation of thermal properties of NAP to propose a mechanism of its thermal behavior. The results obtained by TG/DTG in N2 presented a single mass loss step, assigned to the decomposition of the drug between 153.5 and 305.2 °C, without residue at the end of the run. In DTA curve, it was observed a sharp endothermic peak related to melting of NAP, at 156.6 °C. Others endothermic and exothermic peaks were also observed, associated to the decomposition process. DSC curves of NAP were recorded in the heat-cool-heat mode. In the first heating a sharp endothermic melting peak was observed at 156.7 °C. In the cooling cycle it was observed one exothermic peak at 99.0 °C representing the recrystallization of the drug. During the second heating an endothermic peak at 154.8 °C suggests the reversibility of this process. Therefore, it was calculate the first heat ΔfusH = 31.57 kJ mol-1 / ΔfusS = 73.44 J K-1 mol-1 and second heat ΔfusH = 29.49 kJ mol-1 / ΔfusS = 68.92 J K-1 mol-1, revealing less crystallinity in the second melting. The gases evolved during heating of naproxen were characterized by TG-FTIR. Thus, high intensities were observed at 65 min, which correspond to 673.2 °C. The interpretation of the spectra was realized using NIST Database and EPA Vapor Phase databases for comparison.[12-13] . Bands related to 2-methoxynaphthalene and propionic acid were clearly observed in the gas phase demonstrating that naproxen decomposes via releasing of these substances. Therefore, the interpretation of data allowed to suggest a proposed mechanism of thermal decomposition.

Acknowledgments
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Physical stability evaluation of carbamazepine

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Keywords: carbamazepine, glass, bioavailability, physical stability

Biopharmaceutics Classification System (BCS) divides drugs into four main classes, depending on their solubility and permeability. Class I consists of pharmaceuticals which are both highly soluble and permeable. Thanks to that, they have great bioavailability and therapeutic efficiency. On the contrary, Class IV gathers pharmaceuticals with low solubility and permeability. A lot of procedures, concerning many different fields of science, need to be performed to improve their bioavailability. Due to that, they are not very interesting candidates for future development. The most attractive class for researchers in the field of chemistry and physics is Class II. Pharmaceuticals belonging to that class has low solubility and high permeability. Improving their solubility and thanks to that bioavailability is one of the most popular issues concerning studies of pharmaceuticals in recent years.

There are many different ways of increasing drugs solubility. They can modify both the physical and chemical state of the substance. The leading techniques used are reduction of particle size, alteration of the crystal structure, preparation of solid dispersions and cocrystals, formation of salts and buffers.

A well-known and widely used technique of solubility enhancement of pharmaceuticals is amorphisation of their structure during rapid cooling. Obtained crystallographic structure lacks the long-range ordering and is called glassy state. Vitrified substances are higher soluble than their crystalline counterparts, however they are also less stable. As pharmaceuticals need to be unchangeable for all manufacturing and storage time, it is of great importance to study their physical stability and kinetics of their recrystallization.

Our work aims at exploring the glassy state of carbamazepine (CBZ) – an antiepileptic drug, belonging to BCS II Class – obtained during rapid cooling. However, crystalline CBZ seems not to be stable below its melting point. Therefore obtaining its glassy form is not trivial. The phase transition sequence of not modified CBZ during cooling and re-heating cycle after pre-heating it above melting point will be presented using thermal analysis techniques such as Differential Scanning Calorimetry (DSC), Thermooptical Analysis (TOA), Fourier Transform Infrared Spectroscopy (FTIR). The stability of not modified CBZ in the vicinity of melting point will be discussed as well as the procedure of obtaining amorphous CBZ without any degradation product.

It will be shown, that CBZ decomposes into iminostilbene (IMB) – toxic derivative of CBZ – even if CBZ is heated just above melting point (~192 oC). DSC thermograms obtained during re-heating CBZ after previous pre-heating and cooling of the sample show that apart from glass softening and cold crystallization also double melting, indicating presence of some additional polymorphic form or other substance takes place. As values of melting points do not agree with melting points of any known polymorphic form of CBZ, it is clear that new polymorph of CBZ has been received during pre-heating- cooling- re-heating cycle or sample decomposes. Some additional measurements involving such techniques as DSC, TGA, POM and FTIR proved, that melting points are characteristic for fusion of eutectic mixture of CBZ and probably IBM. However, to unambiguously identify the product of CBZ degradation some further studies, especially Powder X-ray Diffraction (PXRD), are necessary.

Acknowledgments

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Drug–matrix interactions in aromatic probe molecule loaded responsive hydrogels and implications for drug delivery

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Keywords: STA, TG, DSC, heat of immersion, XRD, NMR

One of the vehicles most frequently considered for targeted and controlled delivery of chemically or medically active species is responsive hydrogels. Such systems are generally triggered by external physical stimuli (temperature, mechanical effect, electromagnetic radiation, electric or magnetic field) or chemical stimuli (solvent conditions: dissolved species, composition, pH, ionic strength). For biomedical applications temperature is a stimulus commonly applied for regulating drug release on account of its physiological relevance. Poly(N-isopropylacrylamide) (PNIPA) has a lower critical solution temperature (LCST) around 34°C in pure water, i.e., close to the temperature of the human body [1]. That is the reason why most thermoresponsive delivery systems are based on PNIPA hydrogels.

This presentation intends to summarize the results achieved on PNIPA – aqueous drug interaction with various test molecules, including phenols [2,3], ibuprofen, dopamine [4,5] and various indole derivatives [6]. Uptake and release experiments, solid state 1H NMR spectroscopy and powder XRD methods were applied to confirm the conclusions from thermoanalytical and calorimetric data.

It was found that the matrix – probe molecule interaction is influenced, among other factors, by the solubility, the functional groups and their position as well as the hydrophilic/hydrophobic properties of the drug.

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Study of the polymorphism of florfenicol by DSC and Calorimetry

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Keywords: polymorphism, enantiotropy, calorimetry, florfenicol

Florfenicol C12H14Cl2FNO4S is widely used in veterinary medicine and aquaculture. Two polymorphic forms called A and B are known, but the relation between these two forms are not known. Characterization of polymorphic forms constitutes an important aspect of drug development. In order to get a better understanding of the behavior of solid florfenicol and the possible evolution of a metastable form to a stable one, a thermodynamic study has been carried out by DSC and calorimetry. The aim of this present study is to elaborate a rigorous application of the heat-of-fusion rule in view to determine if florfenicol presents an enantiotropic transition or a monotropic transition.

Temperature and enthalpy of transition and of fusion of the stable and metastable forms have been measured by DSC (TA Instruments). The main difficulty in this study is due to the fact that the temperature of the three events are very close, by the way it has been necessary to perform measurements at very low heating rate (0.1K/min) in view to separate the three phenomena. On another hand to perform the measurement of the metastable fusion it has been necessary to realize the measurement with a heating rate of 100K/min.

Identification of the two forms has been realized by X-Ray. TGA has been used in view to detect the eventual existence of solvates.

In view to confirm the kind of transition, Cp measurements of the two forms have been performed with a C80 calorimeter (Setaram), with these values, it has been possible to determine the function of the variation of enthalpy versus of the temperature $\Delta H = f(T)$. For this it has been necessary to isolate the two forms. This operation has been realized in the C80 calorimeter used for Cp measurements. Form A, stable at room temperature has been heated up to her temperature of transition and then quickly cooled before the beginning of the fusion, and then Cp measurement of form B has been performed.

It was necessary to proceed by this way because the metastable form B presents a rapid evolution to the stable form A. A study of the kinetic of transformation has been realized and is presented.

In conclusion, it is now proved that the polymorphism is an enantiotropic case, the temperatures and enthalpies of fusions have been determined and the kinetic of transition of the metastable form to the stable form is presented, no solvates have been detected.

Polymers

Thermal properties of rubber compositions with pecan nutshell and compatibilizing agent to retread tires

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Keywords: pecan nutshell, rubber, tire, DMA, OIT

Retreading tires is a way to help the environment by reusing the casing of the tire and placing a new tread. Besides this, for the environment, using natural fillers in substitution of petrochemicals are also prodigious in a formulation for retread tires. This study evaluates the thermal behaviour of rubber compositions to retread tires substituting carbon black to pecan nutshell using a compatibilizing agent. Pecan nutshell, obtained from local farmers who currently discard in the environment, is an interesting material due its composition based on cellulose, hemicellulose and lignin, becoming an environmentally attractive option in substitution to carbon black derived from petrochemicals. Pecan nutshell was milled to 80 mesh and dried to up 1% before use. The addition of compatibilizing agent is recommended when blending natural fibers of polar nature with rubbers that are nonpolar, and the right quantity interfere in the final properties. Bis-(γ-triethoxysilylpropyl)-tetrasulfide (TESPT) was used as a compatibilizing agent in the proportion of 10% and 20% in weight related to pecan nutshell content. Thermal analysis are essential to determine important properties as the time of degradation by thermogravimetry (TG), induction time of oxidation (OIT) by differential scanning calorimetry (DSC) and rolling resistance by dynamic mechanic analysis (DMA), for application in tire retreads. The studied formulations include samples with 5 phr (parts per hundred rubber) of nutshell with 10% of TESPT (PCN 5_S0,5), 5 phr of nutshell with 20% of TESPT (PCN 5_S1), 10 phr of nutshell with 10% of TESPT (PCN 10_S1), 10 phr of nutshell with 20% of TESPT (PCN 10_S2) compared with a sample without nutshell/TESPT (PCN 0_S0). Through the TG results it was observed that the presence of nutshell powder, regardless of TESPT, causes reduction in the thermal stability of the compounds, evidenced by the values of T5% of mass loss, wich for the samples PCN 0_S0, PCN 5_S0,5, PCN 5_S1, PCN 10_S1, PCN 10_S2 were, respectively, 341.02°C, 327.26°C, 324.52°C, 310.74°C, 318.76°C. Through OIT results obtained by DSC, it is observed that the samples with 10 phr of nutshell powder and 20% of TESPT show a higher time of induction to oxidation, near the double of the time compared with the sample without nutshell/TESPT, indicating that the nutshell improves the antioxidant properties justified by the presence of lignin, and the quantity of TESPT further strengthens the results. The DMA tests show that the presence of 5 or 10 phr of nutshell and specifically 20% of TESPT reduced in approximately 10% the

tan delta at 60°C, which indicates a lower rolling resistance of the tires. This great result is wondrous for the environment because reduce the pollution, the consumption of gas and the use of petrochemicals.

Acknowledgments

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Kinetics and Degradation mechanism of $CaSO_4{\cdot}2H_2O$ crystals isolated after the Inhibition effect of Maleic-anhydride polymer

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Keywords: Maleic-anhydride polymers; Thermal degradation; Kinetics and mechanism; $CaSO_4$ scales; SEM studies.

This work evaluates the thermal degradation kinetic parameters of $CaSO_4{\cdot}2H_2O$ scales formed in the presence of Maleic-anhydride based polymer (CSS). Pyrolysis experiments were carried out at four heating rates (5, 10, 15 and 200C/min). Several analytical model-free methods were used to determine the kinetic parameters. The Criado model fitting method based on real mechanism followed in thermal degradation of complex has been applied to explain degradation mechanism of CSS.

In addition, simple dynamic model was proposed for successive decomposition of CSS. The model developed enabled the assessment of pre-exponential factor (A) and apparent activation-energy (E_a) for both stages independently using a mathematical developed expression based on an integral solution.

Further adsorbed YMR-polymer not only reduced the decomposition temperature of CSS compared to pure $CaSO_4.2H_2O$ ($CaSO_4.2H_2O$ scales in absence of YMR-polymer) but also distorted the crystal lattice of the organic complex of $CaSO_4$ precipitates, destroying their compact and regular crystal structures observed from SEM studies.

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Novel microwave assisted synthesis and evaluation of maleic-anhydride copolymers as $CaSO_4 \cdot 2H_2O$ scale inhibitors

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Keywords: Microwave synthesis, $CaSO_4$ scale inhibition, Maleic-anhydride, Carboxylic acids, XRD & SEM studies.

Solvent free microwave synthesized carboxylic acid-maleic anhydride copolymers were investigated for its corrosion inhibition efficiency for carbon steel in oil field brackish water. Understanding of thermal decomposition behaviour of these polymers is essential as it is relatively more difficult to control corrosion at high-temperature, compared to ambient conditions. Hence these polymers were investigated under inert condition by dynamic thermogravimetric analysis (TGA) in the temperature range of 25–600°C at three different heating rates. Several analytical model-free methods were used to determine the kinetic parameters. The structure and morphology of these polymers were characterized by FT-IR and NMR-spectroscopy. The corrosion inhibition property of these polymers was evaluated by weight loss method at varying inhibitor concentrations, temperatures and time. Results showed that these polymers were excellent corrosion inhibitor showing 100% inhibition for 3000 ppm at 30°C, but as the temperature increases to 50°C, inhibition efficiency decreases by 14–19%. Moreover, the time-study showed 100% inhibition at 3000 ppm in 1 day, but after 7 days, the inhibition reduces up to 20%. Thermodynamic parameters were calculated at different temperatures. Scanning electron microscopy (SEM) results revealed that after being treated with these inhibitors the coupon surface was unaffected by corrosion. Therefore, the novel polymers show good anticorrosive properties at 50°C for duration of 7 days.

Acknowledgments

The funding for this project was provided by the Research Administration of Kuwait University under Project No. RE 03/14 and GE 01/07 which is appreciated.

Corrosion efficacy and thermal stability of novel carboxylic-acid copolymers in oil field brackish water

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Keywords: Microwave synthesis, corrosion inhibition, carboxylic acids-maleic anhydride polymers, thermal degradation analysis, SEM studies

Solvent free microwave synthesized carboxylic acid-maleic anhydride copolymers were investigated for its corrosion inhibition efficiency for carbon steel in oil field brackish water. Understanding of thermal decomposition behaviour of these polymers is essential as it is relatively more difficult to control corrosion at high-temperature, compared to ambient conditions. Hence these polymers were investigated under inert condition by dynamic thermogravimetric analysis (TGA) in the temperature range of 25–600°C at three different heating rates. Several analytical model-free methods were used to determine the kinetic parameters. The structure and morphology of these polymers were characterized by FT-IR and NMR-spectroscopy. The corrosion inhibition property of these polymers was evaluated by weight loss method at varying inhibitor concentrations, temperatures and time. Results showed that these polymers were excellent corrosion inhibitor showing 100% inhibition for 3000ppm at 30°C, but as the temperature increases to 50°C, inhibition efficiency decreases by 14–19%. Moreover, the time-study showed 100% inhibition at 3000ppm in 1 day, but after 7 days, the inhibition reduces up to 20%. Thermodynamic parameters were calculated at different temperatures. Scanning electron microscopy (SEM) results revealed that after being treated with these inhibitors the coupon surface was unaffected by corrosion. Therefore, the novel polymers show good anticorrosive properties at 50 °C for duration of 7 days.

Acknowledgments

The funding for this project was provided by the Research Administration of Kuwait University under Project No. RE 03/14 which is appreciated.

Thermal degradation of common feed thermoplastics for fused deposition modelling

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Keywords: theral degradation, PLA, Nylon, PVA

Several 3D-printing techniques are very popular nowadays. Among them, fused deposition modelling (FDM) with feed thermoplastic materials is a widely spread manufacturing technique due to its high versatility combined with a relatively low cost. One of the most common problems associated to the use of FDM-printers is the accumulation of residue into or around the extruder nozzle. The accumulation into the nozzle can be easily related to non-oxidizing thermal degradation, while the deposition around the nozzle may involve oxidative processes. However, while cleaning of external deposits is normally easy, removal of internal deposits is much more time consuming. Thermogravimetric analysis (TG) can be used to evaluate and minimize the problems related to thermal degradation of these materials. In this work, a few of the most common, commercially available, feed materials are studied in non-oxidizing conditions by TG. The reaction rate in isothermal conditions is investigated at several temperatures and a kinetic description is proposed. In addition, the amount of char and inorganic residue generated by each material should be considered for better performance. The results presented here will be complemented by a rheological study to be presented in a new article.

Acknowledgments

This research has been supported by the Spanish Ministry of Science and Innovation, MINECO MTM2017–82724-R grant, Xunta de Galicia (Centro Singular de Investigación de Galicia accreditation [ED431G/01 2016–2019] and Grupos de Referencia Competitiva [ED431C2016–015]). These grants are cofunded by the European Union (European Regional Development Fund – ERDF).

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Thermal behavior and phase structure in low density polyethylene – dimethyl terephthalate mixtures studied by differential scanning calorimetry and optical methods

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Keywords: low density polyethylene, dimethyl terephthalate, phase diagram, differential scanning calorimetry, phase structure

Based on the concept that treats semicrystalline (SC) polymers as internally stressed (metastable) spatially structured liquids with crystallites as crosslinks of the intermacromolecular network [1, 2], phase diagram for the low density polyethylene (LDPE) – dimethyl terephthalate (DMTP) system (see Fig.) was constructed for the first time using an original optical method. Analysis of its topology enables one to conclude that this diagram belongs to the type combining peculiarities of SC polymer – low molecular mass crystalline substance and SC polymer – thermodynamically poor solvent systems Contrary to the literature data obtained by less precise differential scanning calorimetry (DSC) method for high density polyethylene – DMTP mixture [3], the present diagram contains the binodal fragments EG and HF and boundary line BD. The latter drastically changes thermodynamic meaning of the diagram and interpretation of the phase structure at different points on the diagram. In order to evaluate the efficiency of substantially less laborious DSC method, which takes 5 days instead of 150 days by the optical method, heating, cooling and second heating thermograms were recorded. Second heating provided an increase in the interphase area and thus accelerated the diffusion processes.

In the presentation, we carry out the thermodynamic analysis of the phase diagram constructed by the optical method; interpret the images by hot stage microsope to describe the phase structure evolution in the course of cooling down the homogenized blends; discuss the DSC thermograms along with assumptions usually accepted in their analysis; compare the DSC and optical data to estimate the DSC efficiency for studying phase equilibrium and structure of the chosen system.

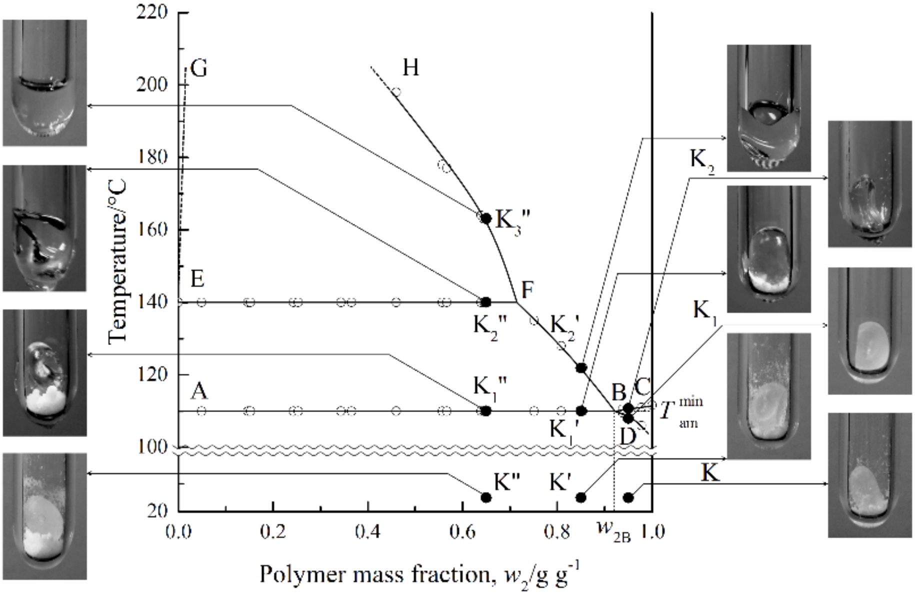

Fig. Phase diagram for the LDPE/DMTP system together with photographs reflecting the state of the system at K – K_3" points.

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Study of thermal decomposition of copolymers of polyethylene glycol phumarate with acrylic acid

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Keywords: unsaturated polyester resin, acrylic acid, polyethylene glycol fumarate, copolymer, activation energy

Intensive development of fundamental research in the field of radical copolymerization, which allows regulating the properties, structure, molecular weight of copolymers and process velocity, dictates the task of finding new monomers for synthesizing polymers with a wide range of practically valuable properties. From this point of view, unsaturated polyester resins are of considerable interest. They are easily copolymerized with vinyl monomers. The concept of "copolymerization of unsaturated polyester resins" was first introduced into the chemistry of polymerization processes by Benig [1]. The ability to copolymerize polyester resins with vinyl monomers, for example, with styrene, was discovered in the middle of the 20th century [2].

Unsaturated polyester resins based on maleates and fumarates hardened with vinyl monomers have specific physico-chemical and physico-mechanical properties [1-4].

Solutions of unsaturated polyester resins in vinyl monomers have low viscosity, and the presence of unsaturated bonds at low temperatures contributes to the formation of spatially cross-linked copolymers [5-6], which can be used as ion exchangers, polymer substrates nanocatalysts, sealants, and adhesives.

This paper presents data on the study of the thermal stability of copolymers depending on the composition of the copolymers. The thermal decomposition of polyethylene glycol fumarate copolymers with acrylic acid of different composition was studied by dynamic thermogravimetry at different heating rates in inert gas. Experimental data processed by the graphical methods of Friedman, Flynn-Ozawa-Walla and Kissinger-Akahir-Sunoz allowed to calculate some kinetic parameters of the process (Table 1).

Table1. Energy parameters of decomposition of polyethylene glycol fumarate copolymers with acrylic acid of different composition

The composition of the copolymers, mol %	**Calculation methods, kJ / mol**		
	Flynn-Ozawa-Wall	**Friedman**	**Kissinger-Akahir-Sunoz**
10/90	219.27	228.20	219.62
25/75	227.08	233.32	227.54
50/50	270.78	279.37	273.99
75/25	246.92	254.28	248.91
90/10	201.87	206.93	201.58

As follows from the table, the dependence of the activation energy on the composition of the copolymers is of an extreme nature. Copolymers with equal content of monomers have a high value of activation energy, to determine the reasons for further research.

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Low temperature behaviour of metachylate based pour point depressants

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Keywords: pour point, lubricating oil, methacrylate, DSC

Base oils are widely used in different types of engines in order to lower the friction between the moving parts. Usually their basic properties like viscosity, pour point, anti-corrosion are improved by the addition of different additives. One type of such additives is methacrylate based pour point additive. They are easily manufactured by the free radical copolymerization of corresponding methacrylate monomers in solution of lubricating base oil. Therefore, they can be chemically modified relatively simply by the addition of different functional methacrylate comonomers due to similar copolymerization reactivity. This is their noteworthy advantage over competing additives. In this work polymer additives with different composition (methyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, N,N-dimethylaminoethyl, styrene) and molar mass were synthetized. Influence of the composition and molar mass on pour point properties was studied in different base oils by ISO 3016 method and differential scanning calorimetry. Results indicate unambiguous correlation between composition of polymers and crystallization maximum/ enthalpy obtained by DSC. DSC crystallization maxima of polymers has a same trend as pour point results obtained for 0.5 wt% solutions of polymers in base oil. At lower concentration of additives (0.1, 0.5 wt%) there is a noticeable change in DSC curve but in most cases there is a low or no correlation between composition and crystallization maximum/enthalpy. This indicates that beside composition intra- and intermolecular interactions in polymer solution and their influence on the solution viscosity, solubility of the polymer, hydrodynamic volume of the polymer coil have a noticeable effect on overall crystallization behaviour. Obtained polymer additives have a positive effect when added in lubricating oils which results in lowering the pour point up to 30 °C. Thermal stability was assessed by thermogravimetric analysis and has shown that in case of methacrylate terpolymers, decrease in molecular weight of polymer increases the thermal stability, while in the case of styrene-methacrylate terpolymers, decrease in the polymer molecular mass has almost no effect.

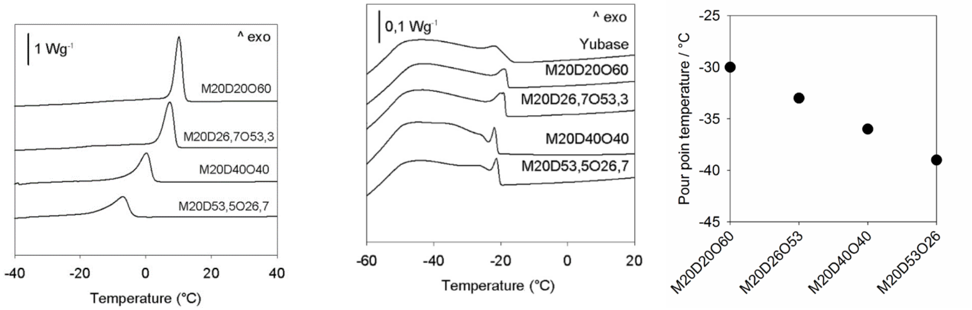

Fig. 1. From left to right: DSC curve of terpolymers, DSC curve of 0.5 wt% solution of terpolymers in base oil and pour point temperature of 0.5 wt% solution of terpolymers in base oil

Determination of the short time stability of polymers by fast scanning calorimetry

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Keywords: SECA, fast scanning calorimetry, selective laser sintering

Thermographimetric Analysis (TGA) is a standard method to measure the thermal stability of polymeric materials. This technique is not sensible for degradation steps which are not related with mass loss. However, such reactions can significantly influence the mechanical behavior of material. Here, the technique of stability estimation by crystallization analysis (SECA) and pseudo TGA which uses differential scanning calorimetry is shown. SECA measures the influence of decomposition on crystallization kinetics. This technique is very sensitive to decomposition. Using fast scanning calorimetry, SECA determines the short time thermal stability of semi-crystalline polymers. This property is essential for fast polymer processing like laser sintering or welding. Investigations are carried out on different materials developed for selective laser sintering like polyamides, thermoplastic elastomers and poly (ether etherketone).

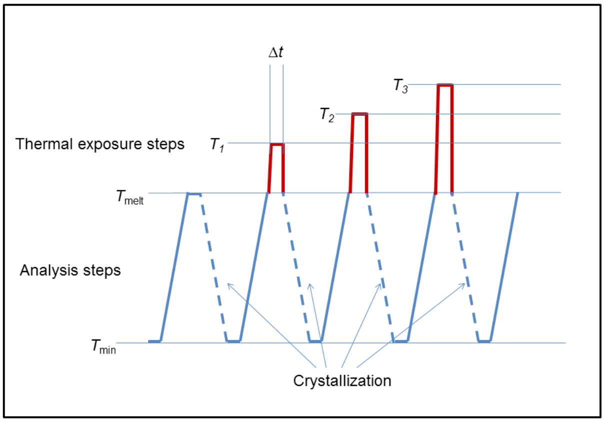

Fig. 1: SECA: Stability Estimation by Crystallization Analysis

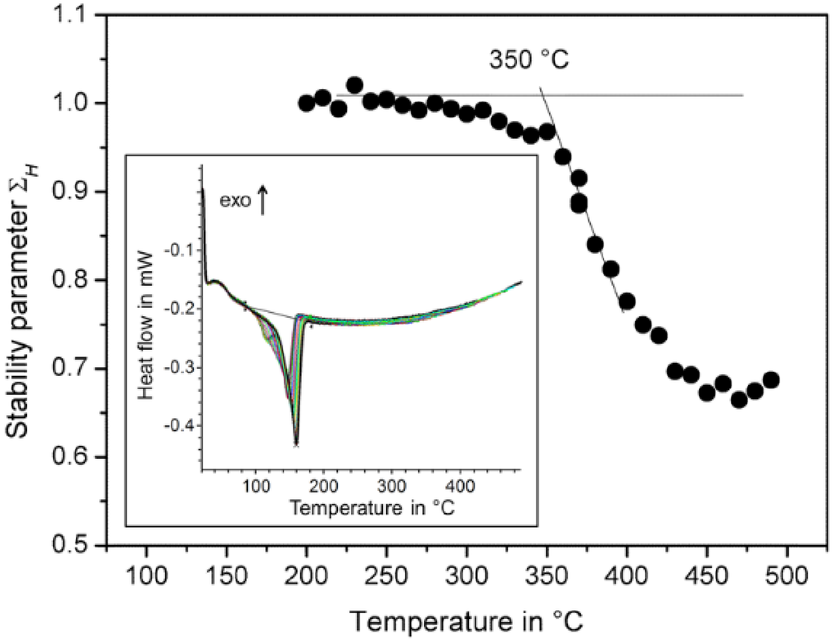

Fig. 2: SECA of Polyamide 12

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Flash DSC study on the low-temperature crystal nucleation in the blends of poly(lactic acids)

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Keywords: crystal nucleation, low temperature, blends, poly(lactic acids)

We employed the commercial chip-calorimeter Flash DSC 1 to investigate the crystal nucleation behaviors of symmetric and asymmetric blends of poly (lactic acids) with the molecular weight of 20 kg/mol at the low temperature (down to 35 degree C of depth below glass transition temperature Tg). The results show that crystal nucleation below Tg can accelerate crystallization rates at higher temperatures. Such acceleration can be attributed to the special interactions of stereo-complex crystals, because homo-crystal in pure polylactic acid does not show such an effect. In the case of asymmetric blends (PDLA/PLLA 3:7), crystal nucleation at 30 degree C and at 40 degree C separately accelerates and retards crystallization rates by one order of magnitude at 110 degree C. This contrast can be attributed to the formation of stereo-complex crystals at 30 degree C but homo-crystals at 40 degree C.

Acknowledgments

Thanks National Natural Science Foundation of China (Grant No. 21474050 and 21734005) for financial support.

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Flash DSC study on polymer crystallization kinetics

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Keywords: Flash DSC, crystallization kinetics, polymers

Fast-scan chip-calorimetry represents a new and rapid development in DSC measurements, which has pushed forward the research frontier in the field of polymer crystallization. We employed the commercialized apparatus Flash DSC 1 to investigate crystallization kinetics of several polymers, including polypropylenes, polyamides and polyketones. The results provide our confidence on this new approach facilitating our better understanding of the basic crystallization mechanisms in polymers with various featured chemical structures.

Acknowledgments

The support from National Natural Science Foundation of China (No. 21734005) and Ministry of Science and Technology of China (Sino-Romania Collaboration Project) is appreciated.

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Corrosion efficacy and thermal stability of novel carboxylic-acid copolymers in oil field brackish water

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Keywords: Microwave synthesis, Corrosion inhibition, Carboxylic acids-maleic anhydride polymers, Thermal degradation analysis, SEM studies

Solvent free microwave synthesized carboxylic acid-maleic anhydride copolymers were investigated for its corrosion inhibition efficiency for carbon steel in oil field brackish water. Understanding of thermal decomposition behaviour of these polymers is essential as it is relatively more difficult to control corrosion at high-temperature, compared to ambient conditions. Hence these polymers were investigated under inert condition by dynamic thermogravimetric analysis (TGA) in the temperature range of 25–600°C at three different heating rates. Several analytical model-free methods were used to determine the kinetic parameters. The structure and morphology of these polymers were characterized by FT-IR and NMR-spectroscopy. The corrosion inhibition property of these polymers was evaluated by weight loss method at varying inhibitor concentrations, temperatures and time. Results showed that these polymers were excellent corrosion inhibitor showing 100% inhibition for 3000ppm at 30°C, but as the temperature increases to 50°C, inhibition efficiency decreases by 14–19%. Moreover, the time-study showed 100% inhibition at 3000ppm in 1 day, but after 7 days, the inhibition reduces up to 20%. Thermodynamic parameters were calculated at different temperatures. Scanning electron microscopy (SEM) results revealed that after being treated with these inhibitors the coupon surface was unaffected by corrosion. Therefore, the novel polymers show good anticorrosive properties at 50°C for duration of 7 days.

Acknowledgments
The funding for this project was provided by the Research Administration of Kuwait University under Project No. RE 03/14 which is appreciated.

Fundamental aspect for the evaluation of activation energy of thermal degradation of fluorine containing elastomer by TGA

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Keywords: TGA, derivative of TG curve, weight change at constant temperature, activation energy, fluorine containing elastomer

Introduction: The activation energy of thermal degradation of polymer is one of the important factors for the short time test of the sample. This article compared the activation energy obtained by the constant temperature method and by TG.

Experimental: The sample used in this study was tetrafluoroethylene-propylene copolymer whose thickness was 0.15 mm. The thermal aging at constant temperature was performed in an air oven controlled at the constant temperature from 240°C to 300°C. The weight of the pan with sample was measured periodically by chemical balance at room temperature. TG curve was obtained using TG 8120 (Rigaku Co.) with supplying air in the heating head. The rate of temperature rise was from 0.033 K/min to 10 K/min.

Result and discussion: The activation energy obtained by the measurement at constant temperature was 110-123 kJ/mol. TG curves was analysed by the methods of Ozawa T [1] and Flynn J. H. and L.A. Wall [2]. The activation energy obtained depended on the rate of temperature rise as shown in Table 1. The activation energy obtained by constant temperature method and that obtained by TGA was greatly different each other. The article studied the temperature at which weight started to increase and the inflection point as an index of thermal aging, which definition is shown in Figure 1. The Arrhenius plot of two indexes is shown in figure 2. Both activation energies were higher than that obtained by constant temperature method. The results suggested that the TG of lower temperature rise rate might be useful to decide the accurate activation energy of this sample.

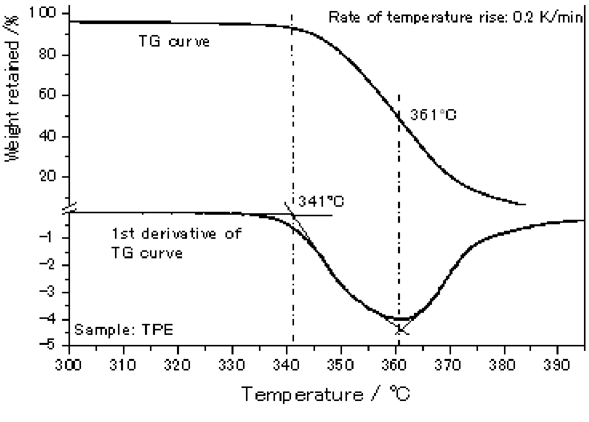

Fig.1 Definition of weight started to decrease and inflection point

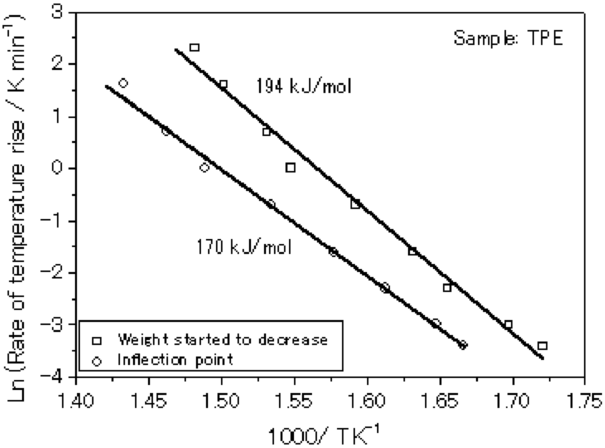

Fig.2 Arrhenius plot of weight started to decrease and inflection point

Table 1 Activation energy obtained by various methods

Observed point	Activation energy /kJ mol^{-1}
Thermal aging at constant temperature	110–123
TGA, rate of temperature rise was 0.5 K/min-10 K/min	219–237
TGA, rate of temperature rise was 0.033 K/nin-0.5 K/min	153–173
TGA, weight started to decrease	186
TGA, inflection point (Second derivative is 0)	170

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Viscoelastic behavior of silicones with different crosslinking density

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Keywords: silicones, crosslinking density, rheology, thermal analysis, viscoelasticity

Silicones consist of a silicon-oxygen backbone with organic groups, typically methyl groups. The organic side groups can be used to link two or more chains together. It is well known that the variation of the Si-O chain length, among other features, such as side groups and the chosen crosslinker allow to obtain silicones with properties ranging from liquids to hard plastics [1]. The aim of this work is to study the influence of temperature and molecular length of vinyl-terminated polydimethylsiloxanes (VTPDMS) on the viscoelastic properties of different silicones. These silicones have been obtained from mixing VTPDMS and poly(dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated as crosslinker. Samples with different crosslinking densities were prepared using a 1.5 hydride to vinyl ratio. All samples were tested on tested on a rheometer using the parallel plate geometry. Tests consisted of strain and frequency sweeps, which were performed in isothermal conditions at different temperatures. The influence of each variable on the viscoleastic response has been evaluated and modeled using qualitative and quantitative analysis.

Acknowledgments

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Evaluating the flame retardancy and thermal stabilizing effects of an organophosphate on polystyrene

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Keywords: Bis(2,4-dicumylphenyl)pentaerythritol diphosphate, flammability, PS, Thermal stability, Degradation kinetic, Friedman, Kissinger

Polymer Matrix Composites (PMCs) are one of the most important classes of engineered materials which have found extensive applications due to favorable properties such as high strength, lightweight, corrosion resistance, ease of forming etc. However due to the high flammability and low thermal stability of the polymer matrix, careful engineering of PMCs is a necessity for them to conform to fire/heat standards in the various industries of applications. In this work the flame retardancy and thermal stabilization effects of an organo-phosphate, Bis(2,4-dicumylphenyl)pentaerythritol diphosphate (DPP), on polystyrene (PS) was evaluated. PS was compounded with DPP using the melt blending procedure. Thermal stability measurements were done via thermogravimetric analysis, while flammability studies were conducted via cone calorimetry and pyrolysis combustion flow calorimetry. By using peak heat release rate as a measure of the intensity of the fine, cone calorimetry measurements indicated that at a loading of 10 mass%, DPP resulted in 22% reduction in PHRR which was more than 3 times the reduction at 5 mass% loading. The 10 mass% composite also showed more than 60% reduction in smoke production. There was no observed correlation between pyrolysis combustion flow calorimetry and cone calorimetry results. Thermogravimetry results indicated that there was substantial improvements in the thermal stability of PS that was compounded with 10 mass% of DPP with $\Delta T50$ being 21°C. To have a better understanding of the effects of DPP on the thermal stability of PS, degradation kinetic studies were carried out on a polystyrene/DPP composite (PS-DPP) with a DPP loading of 10 mass%. Results indicated that DPP had a destabilization effect at low temperatures with corresponding low Ea values when compared with pure PS. A comparative degradation kinetic analysis was performed employing the Kissinger method and the isoconversional methods of Friedman, Starink and Advanced Isoconversional Method (AICM). Variation of activation energy with extent of conversion (α) results from all the isoconversional methods showed that activation energies did not vary significantly with α for pure PS. The activation energy for pure PS had an average value of 180 kJ mol^{-1}. Ea values obtained from the Starink method beyond the destabilization region were very close to those obtained from AICM consistent with Ea values not varying significantly with α for the composite with an average value of 202kJ mol^{-1}. The $y(\alpha)$ and the $z(\alpha)$ master plots together with the Friedman method where used to identify the reaction model and calculate the frequency factor respectively. The Sestak-Berggren model was identified as the most appropriate model to describe the thermal degradation of both PS

and PS-DPP. The overall results indicates that Ea values of the composite were lower than those of pure PS at low conversion where DPP had a destabilizing effect but became higher when DPP had a stabilization effect.

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Thermal and spectroscopic evaluation of the applicability of biopolymers for pharmaceutical and engineering purposes

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Keywords: MDSC, Raman, amorphous solid dispersion, pharmaceutical, PLA, fibres

Biopolymer systems, that gained recently increasing ground in various industry segments, have to be adjusted to certain processing and application requirements. Structural and processing optimization could be performed with combined investigation of biopolymers by thermal and spectroscopic methods, including temperature-modulated DSC (MDSC), thermal gravimetry, cone calorimetry, X-ray diffractometry (XRD), Fourier-transform infrared (FTIR) spectroscopy and Raman spectrometry. Modulated DSC (TOPEM) proved to be especially useful at development of pharmaceuticals of increased bioavailability and lightweight multiphase materials. Pharmaceutical biopolymers are widely used for forming amorphous solid dispersions created to enhance the dissolution of active pharmaceutical ingredients of poor bioavailability. These are usually binary or ternary compositions with at least a drug and a polymer incorporated. Modulated DSC could be successfully applied at separating the thermal events of the individual components, even frequency independent and dependent ones [1]. Furthermore, glass transition temperatures (Tg) – that are sometimes remaining hidden with normal DSC – could be detected revealing the separated phases. These amorphous solid dispersions must be processed into different formulations such as granules or tablets. This means the addition of further components increasing the complexity of the system. During this processing, the probability of phase separation and crystallization of the amorphous drug is enhanced. Therefore, the combined application of sensitive thermal analysis and spectrometry (Raman) tools to reveal these undesired events can be a key to successful developments. Poly(lactic acid) (PLA) is one of the most promising biopolymer applicable – due to its various structural forms – from pharmaceutical through packaging to engineering purposes [2]. In the present work, PLA fibers, nanofibers and foams have been prepared by different methods such as electrospinning or supercritical CO2-assisted melt extrusion. When producing PLA fibers, the special dimensions give the material a number of advantageous attributes, which we can further optimize by thermal or chemical treatments to meet the application-specific requirements. Thermal annealing (heating the fibers above Tg) or lowering the Tg with a solvent give the opportunity to increase the crystallinity of PLA fibers, extending thus the processing window of hot compression (a popular manufacturing method of self-reinforced composites) [3]. The formation of the more stable alpha and the less stable alpha prime forms of PLA has been evaluated, indicating crucial differences between thermal annealing methods. The effects of different treatments on crystalline and amorphous phases were investigated by DSC, XRD and Raman spectrometry. In order to evaluate the thermal stability of the modified products thermal gravimetry, cone calorimetry and laser pyrolysis FTIR methods were applied too.

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Synthesis and thermal analysis of polynorbornene by mono and dinuclear α–diimine Ni-based catalysts

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Keywords: polynorbornene, dinuclear catalysts, cooperative effect, α–olefins, Ni-based catalysts

Multinuclear catalysts based on late transition metals (LTM) have been investigated by researchers. These structures are symmetric and asymmetric and centers are linked together by rigid and flexible bridges. Each structural parameter including the substituents and backbone showed impact on the behavior and productivity of the catalyst in polymerization route. This issue reveals that how the catalyst performance depends on the steric and electronic effect of the structure, higher activity and commoner incorporation by dinuclear catalyst ascribed through synergistic and cooperative effects, respectively. Mono (MC) and dinuclear (DC) α–diimine catalysts based on Ni were used in polymerization of norbornene. DC catalyst through synergistic effects exhibited higher productivity (1.3×106 g/mol Ni) in comparison to MC catalyst (0.8×106 g/mol Ni) and molecular weights (Mv and Mw) of the polynorbornene (PN) made by DC (5.1–9.0×105 g/mol) were greater than the sample obtained by MC (2.4–4.7×105 g/mol). The greater productivity of the DC catalyst attributed to the optimum bulkiness around the active center and dinuclearity effect leading to the better diffusion and access of monomer into active center. Reaction parameters especially polymerization temperature showed a significant impact on catalyst productivity and molecular weight of the samples. Thermal analysis including DSC, DMTA and TGA employed to characterize the PNs and revealed that the sample obtained by DC catalyst had a much uniform and regularity in microstructure, while for MC, results were slightly different. Based on this, Tg of the PN made by DC catalyst was distinctive, and DTGA curve was unimodal. Microstructural study of PNs were carried out using 13C NMR and confirmed the observed properties.

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Thermal analysis of gelatin/clay nanocomposites solid polymer electrolyte

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A new class of materials containing a nanoscale mixture of silicates and polymers has been studied over the past 40 years due to its industrial importance. These modified materials can be modified resulting in different physical and chemical characteristics regarding the starting materials. In this sense, it is possible to control and improve mechanical, thermochemical, rheological, electrical, and optical properties [1]. Thus, the study of properties of these nanocomposites can be of great help in the development of new materials for specific applications. Many papers describe properties of polymer/silicate nanocomposites, but little attention has been given to nanocomposites based on natural polymers and clays. There is a great advantage in the use of natural polymers, such as low cost, biodegradability, and their abundance in nature. Gelatin is a non-toxic, low-cost, biodegradable base that forms clear, high-viscosity solutions and is a highly effective raw material with a high collagen content. In the present work gelatin/silica nanocomposites were prepared in different formulations in order to investigate their properties as a function of composition. Gelatin/Sca-3l-Na+ and gelatin/Sca-3l-Li+ nanocomposites were prepared by solution intercalation method and characterized X-ray diffraction (XRD) presenting d(001) = 12.3 Å to gelatin/Sca-3l-Li^+ and d(001) = 12.8 Å to gelatin/ Sca-3l-Na^+ with a mostly exfoliated structure. The thermal characterization. SEM images revealed that silica contents from 10–15% (*m/m*) improved the homogeneity regarding the pure gelatin, however 20% (*m/m*) of silica resulted in less homogeneous films. TG/DTG curves of SCa-3-Na^+ of SCa-3-Li^+ clays revealed similar thermal behavior with three mass loss steps: one of dehydration, and related to desidroxylation. Silicates and aluminates are the final residues with *c.a.* 85-87% of the starting mass. Gelatin/Sca-3-Na^+ and gelatin/SCa-3-Li^+nanocomposites presented mass loses due to evolution of adsorbed water, two degradation steps and burn of carbonaceous residues. Mass losses were proportional to the composition of each sample. Temperatures of degradation were similar to those of the pure gelatin. DSC curves presented the dehydration, but do not revealed glass transitions, that are supposed to appear in temperatures near degradation.

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The thermal study of polyurethane/hydroxyapatite/chitosan composites modified with phase change material

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Keywords: polyurethane, chitosan, thermal properties

Polyurethanes are a class of polymers composed of isocyanates and polyols, bonded by a urethane linkage [1]. The polyurethane chains are built from soft segments and hard segments, originating from macrodiol, and diisocyanate and chain extender units, respectively [2]. The soft segments usually show the glass transition temperature below room temperature and allow to preserve good mechanical properties. The hard segments show much higher Tg and melting temperature values [3]. In the body, polyurethane is exposed on action of surrounding tissue fluids and may undergo enzymatic degradation, hydrolysis, chemical degradation, calcification, and oxidation [4]. Chitosan is obtained in the deacetylation process of chitin, a natural polysaccharide composed of d-glucosamine and N-acetyl-d-glucosamine. It is polysaccharide that exhibits similarities to components of natural bone tissue like glycosaminoglycans [5]. The addition of hydroxyapatite can promote bioactivity and cells proliferation [6].

A polyurethanosaccharide composed of hexamethylene diisocyanate (HDI), poly(ethylene glycol) 2000, 1,4-butanediol (BDO) and chitosan with hydroxyapatite (HAp) and phase change material (PCM) has been synthesized via two-step bulk polymerization method, using dibutyltin dilaurate (DBTDL) as a catalyst under nitrogen atmosphere. The thermal properties of the polyurethane-based composites were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and dynamic mechanical analysis (DMA). The incorporation of PCM causes a decrease in glass transition (Tg), deltaCp and the heat of melting of soft segments. The results from TG confirmed the increase of thermal stability with increasing content of PCM and HAp. It is expected that these novel polymer materials may find applications as a replacement of acrylate bone cement.

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Pyrolysis

Thermal degradation behaviour of microwave synthesized anhydride based polymers and its application as corrosion inhibitors

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Keywords: MA-polymers, Microwave synthesis, Thermal degradation behaviour,
Kinetics and mechanism, corrosion inhibition, SEM analysis

This paper presents our research efforts in the discovery of pioneering synthetic routes and designing of low molecular weight maleic-anhydride (MA) based polymers (YMR-series) and its application as corrosion inhibitors. Therefore, in this work for the first time simple, eco-friendly, cost-effective, solvent-free and rapid microwave-assisted method has been developed to synthesize these polymers.

The structural and thermal properties of these polymers were analysed using gel permeation chromatography and thermogravimetric analysis. Pyrolysis experiments were carried out at three heating rates (5, 15 and 200C/min). The thermal degradation behaviour of MA-copolymer is compared with MA-homopolymer. Several analytical model-free methods were used to determine the kinetic parameters. The Criado model fitting method has been applied to explain degradation mechanism of these polymers.

The corrosion inhibition of mild steel in oilfield brackish water has been studied at various concentration and temperature using weight loss method. Results showed that YMR-polymers are excellent corrosion inhibitors and at 900ppm shows inhibition of 93.5% for 300C temperature and 87% inhibition for 500C. The scanning electron micrographs revealed that the coupon surface was unaffected after being treated with these inhibitors, Therefore, it can be concluded that YMR-series polymers are highly effective corrosion inhibitors for cooling water systems.

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Examination of the interference of polymerized styrene butadiene rubber 1502 pyrolysis residues to the identification of gasoline

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Keywords: fire investigation, SBR 1502, TG-DSC, GC-MS, HCA

In fire investigation science, gasoline is a common accelerant produced by petroleum cracking. Therefore, the pyrolysis residues of other petrochemicals may interfere with the identification of gasoline. Polymerized styrene butadiene rubber (SBR) 1502 has combustion characteristics that are highly consistent with gasoline. It has a great influence on the identification results. The pyrolysis process of SBR 1502 was investigated with thermogravimetric-differential scanning calorimetry (TG-DSC), and gas chromatography-mass spectrometer (GC-MS) was used to exam the pyrolysis residues during different stages. The results indicated that SBR 1502 has complete combustion or has a lacking amount, deletion of 2,3-dimethyl naphthalene in pyrolysis residue. However, when SBR 1502 only underwent the first pyrolysis stage or even earlier that did not pyrolyze, the characteristic components in the residue were the same as gasoline, which may interfere with the identification results. Therefore, this study employed hierarchical cluster analysis (HCA) to distinguish between the SBR 1502 and gasoline, and successfully distinguished clearly. The results provide an accurate basis for fire investigations.

Influence of Pd/C, Ru/C and RuPd/C catalysts on lignin analytical pyrolysis connected with GC/MS

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Keywords: lignin; catalysis; pyrolysis; conversion, py-GC/MS

Lignocellulosic materials (biomass, wood) are mainly formed, in addition to other components; by the two most widely found polymers in the world: cellulose and lignin. The presented paper is devoted to the study of processes of thermal degradation of lignin, to the isolation of lignin degradation products, and to the study of the pyrolysis mechanisms at selected temperatures. The study of thermal degradation of lignins was performed by analysing two different liquors obtained by delignification of annual plants and softwood trees. In this work, were first prepared lignin models, which were subsequently used in the analytical pyrolysis study at a temperature range of 300–600°C. The temperature range chosen for pyrolysis was determined by thermal analysis of the prepared lignins. Analytical pyrolysis of lignins was carried out in the presence of the following catalysts: Ru/C, Pd/C and RuPd/C. The yields of lignin pyrolysis decomposition products were in the range of 80-729 mg/g. The greatest yield, 729 mg/g was achieved in the case of lignin pyrolysis of annual plants at 500°C, with the catalyst Ru/C. In case of softwood lignin pyrolysis at 400°C (Pd/C), the yield was 624 mg/g. Phenol derivatives represented a major part of the decomposition products in both cases.

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Thermal decomposition of biomass wastes derived from Palm Oil production

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Keywords: oil palm waste, empty fruit bunch, palm fiber, palm kernel shell, thermogravimetry, pyrolysis

The utilization of renewable energy sources has been promoted for decades with the goal of reducing the level of greenhouse gases in the atmosphere, which causes climate change and other environmental problems. The growing use of biomass as a renewable energy source reduces the dependence on fossil fuels, and decreases the net carbon dioxide emission into the atmosphere because biomass is a carbon-neutral energy source. Biomass can be burnt directly or converted to liquid or gaseous raw materials by thermochemical processes. Biomass wastes, such as by-products of various large-scale industrial processes, are promising feedstock for thermochemical conversion.

The palm oil industry produces large amounts of biomass by-products, which are suitable feedstock for energetic utilization and thermochemical conversion [1]. About 70% of the volume from the processing of fresh fruit bunch is transformed into waste in the form of empty fruit bunches, fibers and shells, as well as liquid effluent. Most palm oil mills generate combined heat and power from fibers and shells, making the operations energy self-efficient. However, the use of palm oil residues can still be optimized in more energy efficient systems.

In this study, we analyzed empty fruit bunch, fiber, and kernel shell derived from the palm oil production process with the aim of utilization of these materials as potential renewable energy feedstock. The specific objective of this work was to obtain information about the composition and the thermal decomposition reactions of these biomass by-products. Furthermore, we studied the effect of low-temperature thermal pretreatments (torrefaction) on the composition of palm oil waste samples to find the optimal torrefaction conditions.

The thermal decomposition of oil palm residues was studied by thermogravimetry (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The biopolymer composition of the samples was determined by acidic hydrolysis, when the carbohydrate components of the samples were decomposed to sugar monomers, and the sugars were analyzed by high-performance liquid chromatography (HPLC). It was established that the chemical compositions of palm fiber and kernel shell are similar, while empty fruit bunch contains higher amount of cellulose and lower amount of lignin. The thermogravimetric curves (TG and DTG) and the product distribution of pyrolysis reflected the compositional differences.

The higher K-content of the empty fruit bunch modified the product distribution due to the well-known catalytic effect of the alkali ions on the decomposition mechanisms of cellulose and lignin [2].

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Physicochemical characterization and kinetic modelling of biochars produced from walnut shells pyrolysis

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Keywords: Biomass residue, walnut shells, thermogravimetric analysis, kintetic modelling

Biochar is an attracting solid fuel posses high percentage of carbon (75 to 82%) and it can be used in boilers, where bagasse or other types of biomass are currently used in boilers [1-4]. A number of authors have studied the physicochemical characteristics of walnut shells and the biooil produced from it [5-7]. However no attention has been made on the biochar produced from the pyrolsys of walnut shells. In the present work, the pyrolysis of different types of walnut shells was performed to produce biochar, i.e. paper (PSW), thin (TSW), medium (MSW) and hard (HSW) shell walnut. The bio-char was prepared in order to understand the effect of variable operational conditions, such as pyrolysis temperature (450–550 °C), and heating (20 °C/min) and nitrogen flow (100 cm^3/min) rates. It is observed that the char yield of different types of walnut shells decreased rapidly with increasing temperature till 550 °Cfor all walnut shells (PSW, TSW, MSW and HSW. The characteristics of four different kinds of walnut shells were determined by analytical method in view of corresponding biochemical constituents (hemicelluloses, cellulose and lignin and extractive). Thermogravimetric analysis (TGA) and kinetics of the different types of bio-char was performed under three different heating rates (5, 10 and 15 °C min−1) in oxidizing atmosphere, to understand the kinetic parameters and reactivity. Kissinger–Akahira–Sunose (KAS), Ozawa–Flynn–Wall (OFW) method were used to find out the kinetic parameters such as pre-exponential factor (A) and activation energy (Ea) using TGA data. The average activation energy of PSW, TSW, MSW and HSW bio-char derived from KAS method are 61.3, 38.8, 73.4, and 73.13 kJ mol−1, respectively, and from OFW method are 58.2, 38.8, 76.4, and 81.19 kJ mol−1, respectively. FTIR analyses clearly showed that there is increase in carbon content while decrease in hydrogen and oxygen contents with an increase in pyrolysis temperature. n addition, aromatic and crystalline nature of the bio chars have been determined with the help of XRD analysis. It is observed from the thermal behaviour and kinetic parameters that the different types of bio-char have potential for energy liberation through various thermo-chemical technologies.

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Experimental investigation of an impinging flame kerosene/Air on an aeronautical composite material

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Keywords: Impinging flame, fireproof test, Composite materials, Thermal degradation, Equivalence ratio

Over the last decades, the use of composite materials is growing for aeronautical applications because of the opportunity to produce lightweight structures reducing fuel consumption and emissions. The growing use of these kind of materials leads to technical and design challenges to comply with safety standards and certifications. Fire safety requirements are especially concerned because fire events became complicated when a polymer composite is involved compared to classical aircraft materials. Indeed, unburned gases and smoke emitted by a burning composite material and the structural degradation can make fire-fighting extremely hazardous [1]. Recently, the European Aviation Safety Agency (EASA) reported in its 2013 Annual Safety Review that the second most frequent cause of fatal accidents involving aeroplanes was the fire/smoke post-impact cause [2]. This highlights the need to carry out experimental researches to improve our understanding and ability to predict the thermal behaviour of thermo-structural aeronautical composite parts in case of fire event.

Aircraft parts dedicated to firewall applications or located in a designated fire zone shall meet a fireproof requirement. The composite part have therefore to pass fire tests according to ISO 2685 [3] or Federal Aviation Administration (FAA) – AC20-135 [4] standards. Both standards use an oil burner to heat the part within a temperature about of 1100°C during 15 minutes. The oil burner (kerosene-air) operates with a kerosene flow rate of Q_v^Fuel=7.58 l/h and the airflow rate is adjusted to 〚Q〛_v^air=25 l/s to generate a diffusion flame (Equivalence ratio approximately equal to 0.88) with: (i) Flame temperature of 1100 °C measured at 100 mm and (ii) Heat flux of 116 kW/m^2. The flame temperature is measured at 100 mm by a six thermocouples rack. When the temperature is adjusted and stabilized around 1100 °C the heat flux is measured thanks to a specific device where water is circulating along a copper pipe exposed to the flame. The water flow rate and temperature are 226 l/h and 25°C respectively. According to the standards cited above, the minimum temperature increase has to be 5 °C. Figure 1 illustrates an overview of the experimental setup based on the use of an FAA designed NexGen burner. This standardised flame intended to be a realistic scenario of an in-service or post-impact fire event. In order to investigate the burn-through resistance and the thermal behaviour of innovative composite materials (thermosetting and thermoplastic polymers), this experimental protocol is necessary during the development phases of new composite parts such as firewalls or new generation APU (Auxiliary Power Unit) air inlets. A first step in this work is to experiment on large composite flat panels with specific instrumentation such as thermocouples installed on different positions to monitor their temperatures distribution. Other parameters such as the degradation rate and normalized char thickness will be determined in this study. Equivalence ratio effects on thermal effects of an impinging flame kerosene/Air on an aeronautical composite material are also illustrated in this work. The presented experiments will help designers to choose between different materials and design options to avoid critical temperature increases areas and perforation in the composite part during certification fireproof tests. The collected experimental temperatures will be compared to a literature theoretical model [5]. This model considers a 1D heat conduction equation with pyrolysis and the diffusion of decomposition gases phenomena.

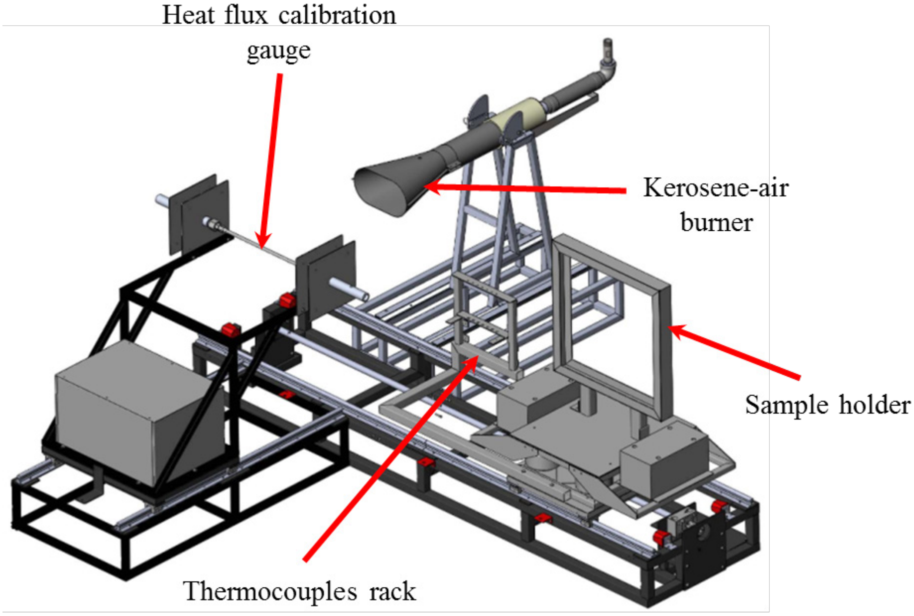

Figure 1. Schematic overview of the test bench.

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Pyrolytic conversion of carbon fibre reinforced composities to recover carbon fibres

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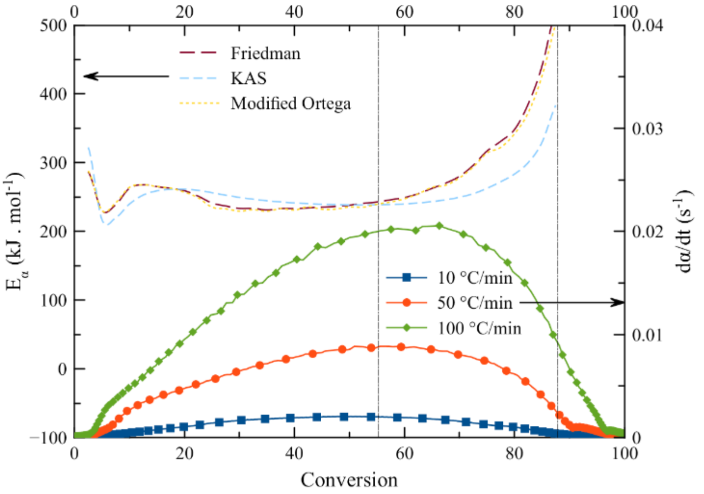
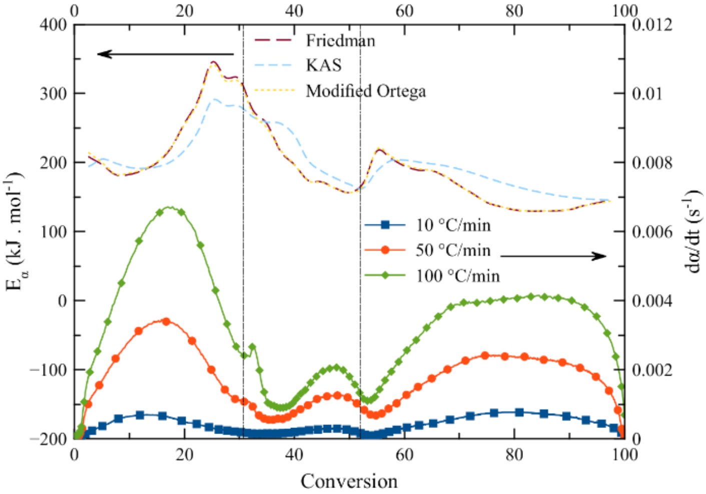
Keywords: pyrolysis, carbon fibre, composites, kinetics, end-of-life

Being light weight, carbon fibre reinforced composites (CFRC) find many applications as a structural material in automobiles, wind turbine blades, polls, boats and ships etc. The amount of CFRC reaching end-of-life (EoL) is increasing tremendously which is causing enormous solid-waste handling and conversion issues. In this study, thermal conversion of CFRC was carried out in a thermogravimetric analyser. Thermal behaviour was studied during non-isothermal heating at 5, 50 and 100 °C/min from 30–945 °C in an inert and oxidative environment. Model-free methods such as Friedman, Kissinger-Akahira (KAS) and modified Ortega were used to calculate activation energy during the course of conversion. The degradation behaviour in the inert atmosphere was identified with a single active conversion zone of temperature ranging between 550 K and 750 K. Most of the polymer matrix decomposed during this zone leaving behind carbon fibres solids. The activation energy averaged around 240 kJ/mol until the extent of conversion reached 55%, after which an exponentially increase was observed till the pyrolysis completed. The oxidative degradation was however more complex with stepwise conversions in three distinct regions of temperatures viz 500–700 K (Zone I), 700–900 K (Zone II) and 900–1200 K (Zone III). Zone I sees an increase in activation energy which decreased during Zone II. Activation energy slightly varied in Zone III. The findings of this study will help understand the pyrolysis and gasification of CFRC and facilitate an efficient design of pyrolyser and gasifier.



(a)



(b)

Figure: (a) Pyrolysis and (b) gasification kinetics of carbon fibre reinforced composites.

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Theory and instrumentation

Simple and accurate analytical equation for the thermal expansion of solids

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Keywords: heat capacity, interatomic potentials, solids, thermal expansion

It is custom to use the Grüneisen equation for the discussion of thermal expansion of solids:

$$\beta = \gamma \frac{C_V \chi_T}{V} \quad \text{or} \quad \gamma = \frac{\beta V}{C_V \chi_T}, \qquad (1)$$

where β is the volume expansion, γ is the Grüneisen constant (formerly "constant", now "parameter"), CV is the isochoric heat capacity, χT is the isothermal compressibility of the solid, and V is its molar volume. Equation (1) was derived from thermodynamic considerations after empirical finding of the proportionality between thermal expansion and heat capacity. It was thermodynamic considerations that have introduced compressibility χT and volume V into the Equation. Thus, it is necessary to know three values (β, CV, and χT) as the functions of temperature and one value (V) in order to use the Grüneisen equation.

Alternative approach based on the pair interatomic potential allows one to derive more simple equation:

$$\beta = A \frac{C_V}{U_0 - H} \quad \text{or} \quad A = \frac{\beta (U_0 - H)}{C_V}, \qquad (2)$$

where A is the constant (depends on the interatomic potential), U0 is the energy of formation of the solid at T = 0, and H is the enthalpy (is derived from the heat capacity as a function of temperature). Thus, it is necessary to know two values (β and CV) as the functions of temperature and one value (U0) in order to use new Equation. It ought to be valid for the solids formed by the atoms and molecules with pair interatomic potentials, first of all, rare gas solids.

The comparison of coefficients γ and A for neon derived from the same set of thermophysical data is shown in Figure 1. Both coefficient are not constant and range between limits that are about two times greater for γ. This shows that the new Equation is preferable for direct comparison between thermal expansion and heat capacity.

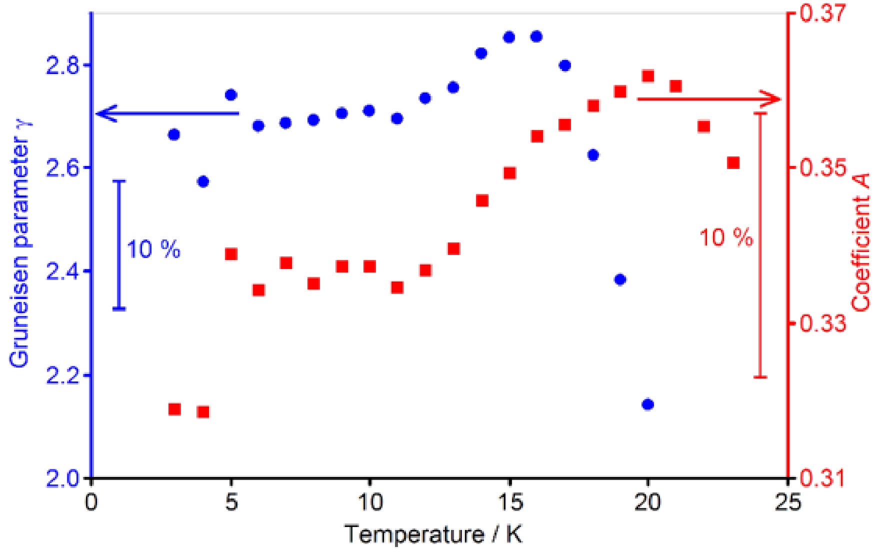

Figure 1. Coefficients γ (circles, left scale) and A (squares, right scale) for neon derived from the same set of thermophysical data after Equations (1) and (2), respectively.

New Equation allows one to derive the thermal expansion of a solid solely after its calorimetric data, contrary to the Grüneisen equation, where additional measurements of bulk modulus are needed.

Isoconversional methods and kinetic parameters: a tool or a goal?

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Keywords: kinetic analysis, activation energy, statistics

Isoconversional methods are routinely employed in kinetic analysis of thermoanalytical data. Ever since late 1950s there is an apparently endless stream of "novel", "advanced", or "improved" methods for obtaining kinetic parameters from non-isothermal measurements based on the general rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp(-E/RT)f(\alpha).$$

However, in practice the differences in the values of kinetic parameters calculated using various methods of the same class (integral or incremental) are often well below their uncertainties and the claimed improvement in the calculation procedures can only be perceived when working with simulated error-free datasets. This is especially true for kinetic studies employing only three or four measurements as statistical analysis of such small-sample measurements using ill-conditioned models based on the Arrhenius equation results in very unreliable values of kinetic parameters. Moreover, the integral methods were shown as inappropriate in the case of conversion-dependent activation energy [1].

It is interesting that such emphasis is placed on determination of kinetic parameters and their fitted values are often viewed as the ultimate result of kinetic analysis. On the other hand, much less effort is devoted to meaningful interpretation and use of these parameters for kinetic modelling. For example, thermal or thermooxidative stability of materials is commonly judged only by comparing the values of the apparent activation energy. This rather popular approach is based on a false assumption that the higher activation energy always implies slower degradation process and thus more stable material (and vice versa).

In this work we demonstrate that the determination of kinetic parameters is merely a "fitting exercise" and the choice of the isoconversional method is not as important as one may have expected. On the other hand, attention should be paid to interpretation of the resulting parameters and their practical implications such as material stability predictions.

Acknowledgments

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McGill Chemistry Characterization (MC_2) facility

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Keywords: facility, instruments, thermal analysis

The McGill Chemistry Characterization (MC_2) facility regroups expert personnel and state of the art instrumentation for the investigation of materials in a wide range of disciplines. The MC_2 is staffed by scientists with expertise in these areas and serve both the experienced and novice investigators by providing training, measurements and/or data interpretation. Here we describe one of our platforms: the Thermal Analysis and Spectroscopy Lab (TAS Lab). What we do and who uses our lab. Beyond research training, we provide support to outside industrial users but also to undergraduate labs. Some examples will be shown.

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Thermal conductivity characterization of enhanced materials: method selection and comparison

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Keywords: thermal conductivity, composite polymers, phase change materials

As material development and research continues to accelerate for enhanced materials such as composite polymers, phase change materials and light weight concrete (to name a few), accurate thermal conductivity characterization is critical to determine the unique heat transfer properties of the specimens. With multiple techniques for thermal conductivity testing available, selecting the correct steady state or transient method plays an important role in the researcher's validation of a new material's performance. No single method is appropriate for all possible samples. Material scientists and engineers working in thermal conductivity improvement and thermal management must therefore develop an understanding of the strengths and weaknesses of the available test methods to select one appropriate to the application.

This study will compare commonly available transient contact methods for different applications of study, including the modified transient plane source technique, the traditional transient plane source technique and the "needle probe" transient line source technique. Appropriate applications for each method will be detailed, and recent research from international institutions pushing the boundaries of thermal conductivity will be highlighted, demonstrating the power of the different methods when used properly for an appropriate sample.

Human body thermal conductance determination using a calorimetric sensor with linear programming of thermostat temperature

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Keywords: direct calorimetry; heat conduction calorimeters; medical calorimetry

The purpose of the calorimetric sensor is to measure the heat flux transmitted by conduction between the human body and a thermostat located inside the sensor. The measurement surface has an area of 2 × 2 cm^2 [1]. We have verified that the measured heat power ($\dot{q}$) varies linearly with the thermostat temperature. This allows us to define a thermal conductance (CT) between the internal temperature of the human body (Tcore) and the temperature of the thermostat (Tthermostat): CT= $\dot{q}$/(Tcore-Tthermostat). This thermal conductance can be determined by measuring the heat flux for different temperatures of the thermostat [2]. An alternative is to perform a single measurement with a linear programming of the thermostat temperature. Fig. 1 shows the heat flux dissipated by the abdomen of a healthy 61-year-old male subject in a resting state, who was dressed normally. The room temperature was 20.7 ºC. Points A and B are the heat flux values obtained with constant thermostat temperatures of 24 and 25 °C, respectively. Curve C shows the transient and the steady states of a measurement made with a linear variation of the thermostat temperature (10 mK/s). The slope of line D allows us to determine the thermal conductance (CT = 17.6 mW/K). The total thermal resistance is the inverse of CT: 56.8 K/W. This value is the sum of the sensor´s thermal resistance and the human body resistance. The sensor´s thermal resistance is determined experimentally (Rsensor = 12 K/W), and the resistance of the human body in this measurement is 44.8 K/W.

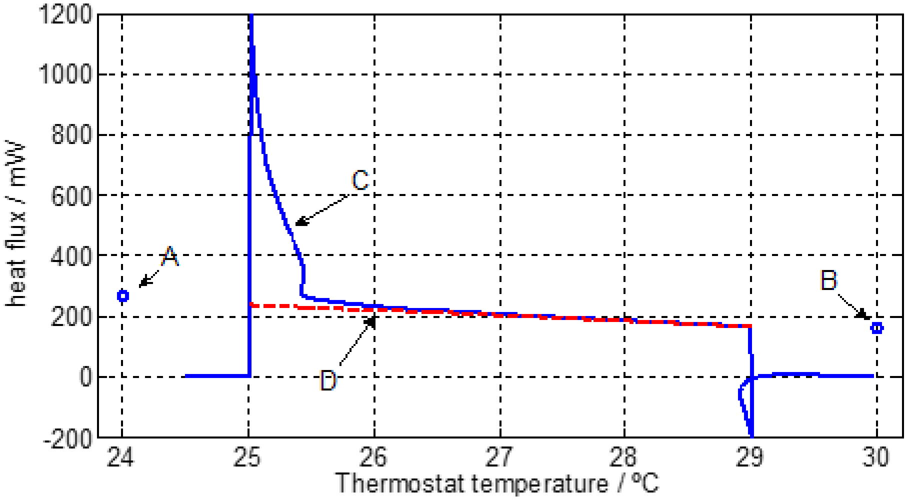

Fig. 1. Thermal conductance determination from a measurement with linear programming of the thermostat temperature (curve C).

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Experimental and Numerical sensitivity study of sources of scatter in quantitative mechanical characterisation of (filled) polymers using DMA equipment

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Keywords: DMA, mechanical properties, thermoplastic, shot fibre composite, repeatability

Dynamic mechanical analysis (DMA) is typically used for thermal analysis, but also quantitative mechanical characterisation should be possible. Due to the typical usage of log scale in presenting the modulus and due to a low number of repetitions, it is rather unknown that a scatter of 20–50% in the absolute measurement values of storage and loss modulus is quite common. For quantitative mechanical measurements, much higher accuracy is required. In a study on the thermoplastic PESU (polyethersulfone), also filled with short glass fibre, the sources of origin of the large scatter were investigated. Next to the known influence of the aspect ratio [1], especially the extreme precision of the sample dimensions was found to define the final result, but also other parameters in the areas of material properties, clamping, heat generation by motor assembly and initial system settings were isolated to determine the influence of every single one. On top of that, finite element simulations and digital image correlation (DIC) were used in addition to the conducted experiments, to study the influence of misalignments, friction, viscoelasticity and relaxation. By focussing on every aspect, it was possible to reduce the error margin on the modulus to less than 5% and guarantee a very high reproducibility of the measurements.

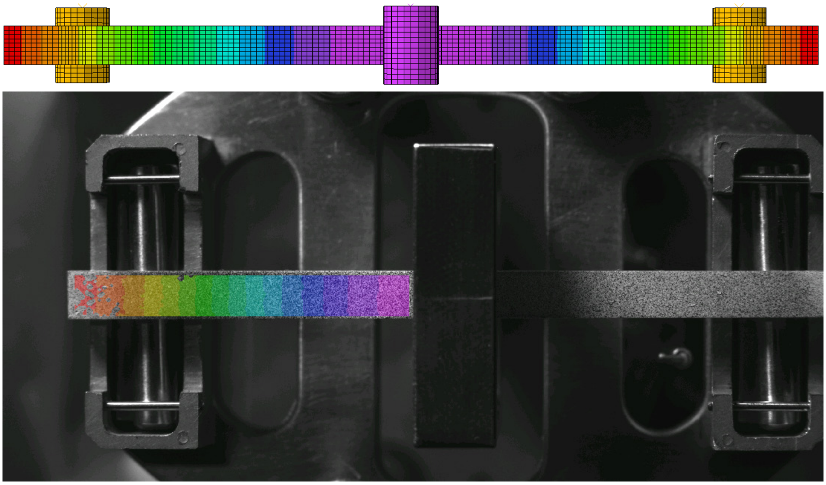

Figure 1: Top view on 3-point-bending clamp with applied deformation. a) FEM simulation. b) DIC experiment

Acknowledgments

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Hyphenation of thermogravimetric analyzers with MS, FTIR and GC-MS

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Keywords: thermogravimetric analysis, mass spectrometry, FTIR spectrometry, gas chromatography, hyphenated techniques

In the field of thermogravimetric analysis (TGA) the attachment of both mass spectrometers (MS) and Fourier transform infrared spectrometers (FTIR) for off-gas analysis has a long history. Both techniques sample and analyze the off-gases in real time, which has distinct advantages for associating detected species with particular mass transitions. A disadvantage exists if there are multiple chemical species associated with a particular mass loss, as they are not chemically separated and therefore identification becomes problematic. Thus many of the uses of TG-MS and TG-FTIR off-gas techniques is for the detection of expected species, not the identification of unknown species. The hyphenating of TGA systems with gas chromatograph – mass spectrometry (GC/MS) systems in essence solves the identification problem, but in the process loses the time/temperature association with specific mass losses. A good thermal analysis laboratory interested in off-gas analysis will thus have multiple hyphenated techniques and may even connect more than one technique to the output of a single TGA. This talk with cover all three instrumental forms of off-gas analysis (MS, FTIR, GC/MS), review the advantages and disadvantages of each, and present relevant data.

Polarisation changes during infrared thermography using silver halide poly-crystalline infrared fiber bundle

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Keywords: optical polarisation, silver halide poly-crystalline, MIR fiber bundles, thermal imaging.

Broadband mid-infrared (MIR) thermography using fibre optic waveguides can be critical in real-time imaging in harsh environments such as additive manufacturing [1, 2], medical diagnosis and therapy [3]. We investigate the polarization effect on thermal measurements through polycrystalline fiber bundle employing a broadband cross-polarization configuration experimental setup. Silver halide polycrystalline fibers AgCl1−xBrx (0≤x≤1) AgClBr-PolyC have very wide transmission bandwidth spanning over the spectral range from 1µm up to 31µm FWHM [3-6]. Moreover, they are non-toxic, non-hygroscopic, with relatively good flexibility over long lengths in meters, which make them very adequate for spectroscopic and thermal measurements in medical and clinical fields [7, 8, 1].

In this study, we used a fiber bundle composed of seven single AgClBr-PolyC fibers, each of them is about 300µm core diameter, inserted between two broadband MIR polarizers. A FLIR thermal camera with a close-up lens was employed to measure the spatial temperature distribution over the fiber-bundle end while focusing thermal light from a Silicon carbide filament source at the entrance of the fiber bundle.

Indeed polarization dependence of temperature measurements has been clearly observed in which the orientation of temperature extrema (minima and maxima) vary from one fiber to another within the bundle. The extrema orientation comply with the broadband cross-polarization configuration showing possible poly crystalline preferential fiber orientation dependency. Therefore, attention should be paid to the assembly procedure of these bundle fibers to ensure consistent measurements.

Acknowledgments

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Computed thermal tomography and 3D IR thermography of buried defects: multiphysics modelling and experimental validation

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Keywords: Thermography, Tomography, Flash thermography, Infrared, Metrology

Over the last decade, IR thermography (IRT) has established its place as a valuable technique for metrology [1–3]. A major industrial use of IRT is the method known as active thermography, which quantitatively delivers dimensional values and thermal diffusivity of not only the surface, but also features within the sample, as heat diffusing from the bulk is affected by variations in structure and material. This allows for defect detection and identification within a sample, from the variation in thermal properties that these defects instigate. This technique finds applications in aerospace, additive manufacturing, welding melts and carbon fibre construction. Combining this techniques ability to image internal defects with the reconstruction technique known as Thermal Computed Tomography (TCT), further insight into the geometries of these internal defects is possible. By imaging and heating a sample from multiple angles, a 3D reconstruction can be achieved to provide 3D-IR thermography (3D-IRT) [3–5].

In this paper, we use a Multiphysics approach in COMSOLTM Platform to develop a finite element model that simulates thermal images obtained in active thermography mode. This approach allows variation in material properties, active thermography methods (Flash, Pulse Phase & Lock-in techniques), source wavelength, depth and dimensions of defect. These simulated images are then reconstructed, allowing for comparative study of the original 3D model used, and the CT reconstructed 3D model. Figure 1 shows the simulated surface temperature (K) of a block with an internal defect, a void, comparing the surface temperature above the void and bulk sample. We then take experimental images of a defect intentionally created in a PLA block to reconstruct for 3D-IRT and validate vis-à-vis the Multiphysics model. Our work shows the feasibility of real time TCT and 3D-IRT of buried defects, which can be hugely beneficial for quality control and process optimisation in additive manufacturing.

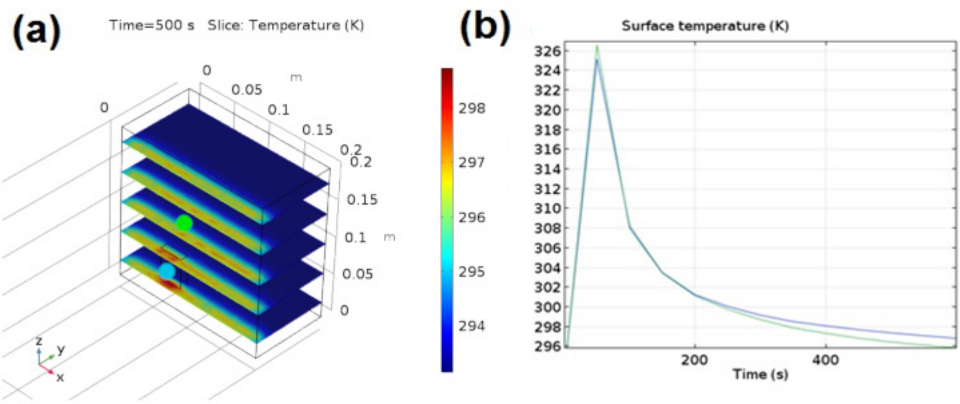

Figure 1. Pulsed flash IR thermography model of a buried defect in PLA polymer block (a) showing the surface temperature (@ 500s) (b) Showing the temperature at two points (green = bulk & blue = void) versus time.

Acknowledgments

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Combustion Calorimetry: yesterday, today and tomorrow

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Keywords: oxygen vessel combustion calorimetry, combustion calorimetry instrumentation, combustion calorimetry applications

Oxygen vessel combustion calorimetry, resembling its current form, appeared in the second half of the 19th century. At the turn of the 20th century it found huge success in industry during mass electrification, when coal consumption skyrocketed. Businesses embraced a tool that allowed the characterization of an energy source by its heat generating ability. Further development of combustion calorimetry techniques and instrumentation continued on two fronts – fundamental thermodynamic research and industrial R&D. Despite significant differences in goals and objectives, advances made in one branch were gradually adopted by the other: new instrument designs, new materials for vessel construction, specialty calorimeters, etc. Combustion calorimetry development in thermodynamic research suffered from declining interest in the second half of the 20th century. However the industrial counterpart continued using advances in the microcontrollers and automation.

Today, combustion calorimetry is a well-established and consolidated domain, with characterized major use cases, and is far from decline. Modern day development is driven by special requests and gradual adoption of advancements in technology. The decades-long dominance of coal testing as the primary use for combustion calorimetry may be over, but the wide scope of other applications has dramatically gained popularity: medical and nutrition research, energetic compounds development, biomass characterization, recycling and waste management, building materials testing, etc. Globalization of markets has led to a usage harmonization, however regional markets still retain their unique aspects.

Balancing user convenience, price, and the suitability of the equipment to a given application has always been a primary driver in the industry. Calorimeter manufacturers offer models for variety of needs including: high-throughput lab testing, occasional standard testing, nonstandard testing, or teaching. Parr also provides customized options for special applications: from calorimeters with access to pressure profile data, to micro vessels for energetic compounds.

Looking forward, the field of combustion calorimetry finds itself in a peculiar position. Despite its maturity, growth into new applications, and many new users, continuity of the tradition seems to have been broken. Thermodynamic research which includes the pillars of theoretical and practical knowledge persists in a dwindling handful of groups around the world, while academia teaches just its most basic concepts. Calorimeter manufacturers, on the other hand, seem to restrict themselves to the codified standard use cases, resulting in the loss of understanding of the mechanisms underlying the methods. Rapid digitalization and user experience with consumer electronics also create misleading expectations that an instrument is a smart black box. The result is concerning: important fundamental details are often overlooked, and users frequently are not aware of combustion calorimetry pitfalls. And those who are, often fail to obtain required advanced knowledge, as well as useful tips and tricks, if they are not available at the click of a mouse.

Industrially-focused combustion calorimetry does not seem to be approaching its sunset, but a changing world brings new demands. On one hand measures must be taken to make knowledge and experience available for general users. At the same time it is a challenge for us, manufacturers, to adapt an old tool to the character of the new generations of digital native users and their expectations.

Thermal hazards, lifetime prediction

Explosion accident of DMPAT and its thermal hazards

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Keywords: thermal decomposition, DMPAT, explosion accident

An explosion accident attributed to thermal decomposition of o,o-dimethyl phosphoramidothioate (DMPAT) resulted in 1 death and 1 injury occurred in Taiwan in 2016. Since the operating data was destroyed in the accident, there is not any information relevant to the developing sequence of the explosion left. This study intends to restore the accident process by the thermal analysis of DMPAT. The thermal hazards of DMPAT were analyzed by PHI-TEC II, ATR, TGA-DSC, DC/MS, and TGA-FTIR. The results of adiabatic calorimeter, PHI-TEC II, show that the onset temperature for the thermal decomposition of DMPAT is 120ºC. The results of TGA-DSC and GC/MS indicated that the vaporized DMPAT reacts with air and release heat at the temperature as low as 50ºC. The heat of reaction for the oxidation of DMPAT vapor is great enough to make the temperature of DMPAT to be greater than 120ºC. The decomposition of DMPAT began at 120ºC, with gas formation and generation of crystalline being observed. The gas formation and generation of crystalline along with the release of a lot of heat became significant as the temperature increased, and the reaction rate became maximum at temperature of 190ºC. The TGA-FTIR and GC/MS indicated that the decomposition gas of DMPAT include methanethiol and dimethyl sulfide, with AIT of both being around 200ºC. The thermal explosion process of the studied accident was summarized as follows. The DMPAT was heated to temperature greater than 50ºC by the external heat source. The released heat of oxidation of DMPAT vapor with air increase the temperature of the liquid phase DMPAT to be greater than 120ºC, onset temperature of DMPAT. The exothermic reaction of DMPAT decomposition not only released great amount of reaction heat but also generated a lot of gas, and made the system to be over pressure, and resulted in thermal explosion. Since the two decomposition gases are flammable and their AIT are both much less than the maximum temperature of decomposition, 300ºC, the gas explosion may also occurred along with the thermal explosion.

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Research on the thermal hazards of Diphenyl methane-4,4’-diisocyanate (MDI)

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Keywords: thermal explosion, MDI, polymerization, bond dissociation energy, excited state, decomposion pathway

Diphenyl methane-4,4’-diisocyanate (MDI) is one of the most important raw materials for polyurethane production. On September 20, 2016, a thermal explosion occurred in a production process of MDI in China killing four people and injuring four others. This study evaluated the thermal hazards of MDI by differential scanning calorimetry (DSC) and thermogravimetric analyser (TG). The exothermic onset temperature and peak temperature of MDI at different heating rates were obtained from TG tests. The thermal decomposition of MDI mixed with water, nitric acid, and sodium hydroxide was measured using DSC. The temperatures in which the pure MDI was polymerized, ranged from 260 to 350 °C at different heating rates. The decomposition reaction of MDI with water, nitric acid, and sodium hydroxide absorbed a huge amount of heat and released CO2. The decomposition reaction temperature at different heating rates ranged from 100 to 150 °C. Gaussian 09 software was adopted to explore the pathway of MDI polymerization to obtain single point energy, zero-point energy, thermal energy, thermal enthalpy, and thermal free energy. The bond dissociation energy (BDEs) at different excited states was calculated. By comparing the BDEs of different excited states, the initial decomposition pathway and the secondary decomposition pathway of MDI polymerization were obtained, and the entire polymerization process was predicted. Combining the experimental and simulation results to formulate safety instructions can provide an effective emergency response in the event of MDI accident.

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Pyrolysis characteristics of materials for 220 kV cable and ignition route analyses

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Keywords: 220 kV cable, Pyrolysis, Ignition route, Waterproof screen layer

The high-voltage electric cable system plays an important role in the urban industry and people's life. However, an unplanned loss of power supply induced by cable fire might bring great trouble to residents. In the past several years, fire accidents happened in the high-voltage electric cable tunnel in China, some of which were induced by the arcing. They make people pay more attention to the fire protection of the high-voltage cable system. The detailed ignition mechanism of powered high-voltage cables is one of the key points.

The objective of this work is to investigate the pyrolysis characteristics of the typical materials for the 220 kV electric cable in China. They are the inner insulator layer, insulated screen layer, waterproof buffer layer and outer sheath layer of the cable. Series of thermogravimetric experiments are carried out for the above four materials. Namely, for each material addressed above, TGA tests are done in the air atmosphere with the heating rates of 5, 10, 15, 25 and 35 K/min, respectively. Figure 1 shows the typical TG and DTG results with the heating rate of 15 K/min. It is suggested that the inner insulator layer, which is normally the XLPE, starts pyrolysis at higher temperatures with a wide and large mass loss rate. However, for the insulated screen and waterproof buffer layers, the pyrolysis temperatures are relatively lower than the insulator and the outer sheath. Especially for the insulated screen, besides the main DTG peak, there are several small DTG peaks at the lower temperatures. It is suggested that the insulated screen material will pyrolysis earlier than other materials of the cable. Therefore, the insulated screen materials in cable might be the weakest point during the ignition by the arcing of the powered high-voltage cable. Finally, based on the Kissinger fitting method, the activated energies of the insulator, insulated screen, waterproof buffer and outer sheath here is 165.35, 153.65, 106.34 and 169.42 kJ/mol, respectively. It is also illustrated again that the activated energy of the insulated screen is obviously smaller than the other three materials. More attention needed to be paid for the fire resistant improvement of the insulated screen material.

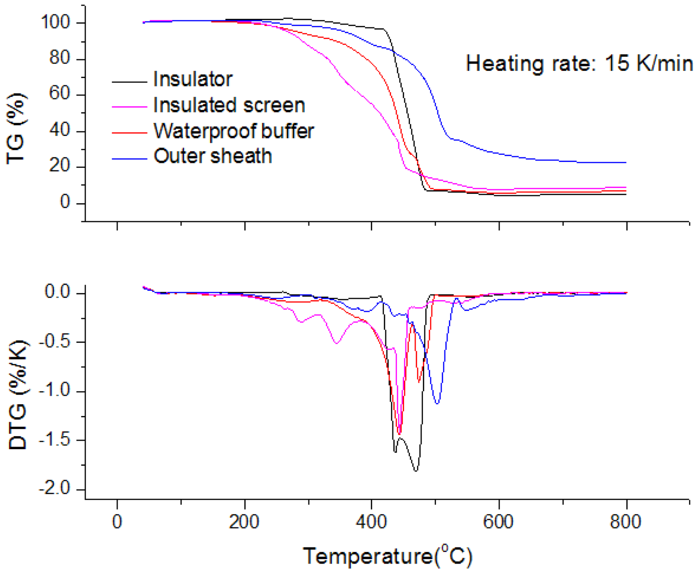

Figure 1 Pyrolysis characteristics of the four materials for the 220 kV single-core cable

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Discuss of some flammability parameters derived from MCC Tests

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Keywords: microscale combustion calorimetry, heat release rate, flammability, derived parameters

Microscale Combustion Calorimetry (MCC) has been developed nearly 20 years, which is D7907, and regarded as a powerful facility to evaluate flammability. Several parameters, such as ignition capacity, heat release capacity, flame spread, fire growth rate, and fire resistance capacity characterizing flammability of materials can be derived from MCC. To study the reliability and uncertainty of these derived parameters, four materials were chosen and 108 samples tested by MCC with 9 heating rates. 5 parameters related to flammability of these materials are derived from test results, algorithms are compared. From the analysis, the robustness and practicability of the parameters and algorithms are evaluated, and new parameters are developed.

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Understanding the hygrothermal aging effects and lifetime prediction on a NASA standard initiator

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Keywords: NASA standard initiator, Hygrothermal aging, Aging-effect, Lifetime prediction, Isoconversional kinetics

The NASA standard initiator utilized in airbags of automobiles or as pyrotechnics in launch vehicles such as rockets and missiles contributes to assuring ignition of the more-difficult-to ignite substances in the system. The designed performance, however, has shown to degrade due to oxidization of metal powder fuel, changes in material properties, and premature reactions in their chemical constituents, all of which contribute to so-called aging process. Earlier studies have focused on the analysis of aging mechanism of the accelerated aging samples at ad-hoc thermal conditions. However, moisture is believed to play an impacting role, and such the role of relative humidity (RH) must be understood as the samples are exposed to the environment of seasonal changes during manufacturing and storage.

The current study is motivated to provide some useful insight into understanding the hygrothermal aging of the zirconium potassium perchlorate (ZPP), better known as a NASA standard initiator. The lifetime of ZPP, heated at 71 oC and exposed to four different RH conditions (0, 30, 70, and 100%), is predicted [1]. The chemical variations in the hygrothermally aged ZPPs were obtained by the X-ray Photoelectron Spectroscopy (XPS). The combustion process and changes in thermodynamic properties such as heat of reaction and activation energy were analysed by utilizing the thermograms of Differential Scanning Calorimetry (DSC) from Mettler-Toledo. Also, the Friedman isoconversional reaction kinetics [2] based on the results of DSC thermograms were constructed by using Advanced Kinetics and Technology Solutions (AKTS) software for the simulation of ZPP combustion. Under hygrothermal aging conditions, ZPP showed decreased heat of reaction with increasing RH or aging duration (Fig. 1(a)). ZPP under the same condition also showed increase in the activation energy (Fig. 1(b)). The results are indicative of shortened lifetime and possible misfire prediction for the initiators exposed to the seasonal storing conditions.

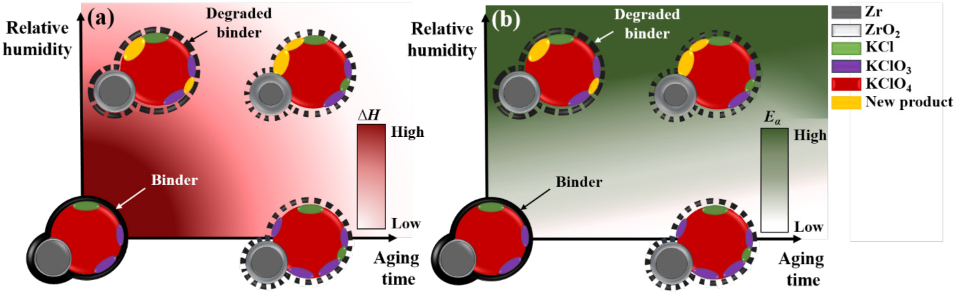

Fig. 1 Illustration of the hygrothermal aging effects on ZPP chemical compound showing (a) decrease in heat of reaction, and (b) increase in activation energy.

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Thermochemistry

Investigations of phase equilibria in LiCl-GdCl3 binary and LiCl-KCl-GdCl3 ternary systems by DTA and XRD

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Keywords: Pyrochemical reprocessing, metallic fuel, ternary phase diagram, DTA, XRD

LiCl-KCl eutectic mixture is used as liquid electrolyte medium in the pyrochemical reprocessing of spent metallic fuel. In this process, fuel elements like U and Pu are selectively electrodeposited in solid and liquid cathodes, respectively [1]. Reactive fission products like alkali, alkaline earth and rare earth metals are dissolved in melt as soluble chloride form. The concentration of the reactive fission products increases progressively with time in the electrorefining process. As a result, the liquidus temperature of the melt increases monotonically. Investigation of phase equilibria of RECl3 with LiCl-KCl melt gives information on the limiting concentration of RECl3 in LiCl-KCl melt, before sending for rare earth partitioning [2]. Systematic experimental study on LiCl-KCl-RECl3 has been carried out in the authors' laboratory [3, 4]. Gd is one of the rare earth fission products having reduction potential close to the actinides in the spent nuclear fuel. Zhou et al. [5] calculated LiCl-KCl-GdCl3 ternary phase diagram using Calphad type optimisation method. Detailed experimental phase diagram is not available on this system. LiCl-KCl binary phase diagram was investigated and assessed by several authors. KCl-GdCl3 binary system was investigated by Seifert et al. [6]. Zheng and Zhao [7] reported the LiCl-GdCl3 binary phase diagram using DTA and XRD techniques. Several thermal events were not ascertained in this system reported by them. In the present work, investigations of the LiCl-GdCl3 binary system and the LiCl-KCl-GdCl3 ternary system by DTA and XRD techniques were taken up.

Large numbers of samples were prepared by mixing high pure LiCl and GdCl3 at 5 mol% interval on LiCl-GdCl3 binary system for DTA experiments. Solidus and liquidus temperatures were deciphered from the heating runs of DTA experiments. The solidus temperatures of the samples were observed at 410 ± 4°C in the LiCl rich side and at 380 ± 4°C in the GdCl3 rich side of the binary diagram. The liquidus temperatures of the samples decreased monotonically from 600°C to 407°C (pure GdCl3 to 40 mol% GdCl3) and increased monotonically up to pure LiCl (605°C). It is indicative of a binary eutectic reaction.

Calculated amounts of high pure LiCl, KCl and GdCl3 were mixed inside high pure argon atmosphere glove box to prepare large number of samples at 10 mol% interval on LiCl-KCl-GdCl3 ternary system DTA experiments. Various thermal events like ternary eutectic, secondary crystallisation and liquidus temperatures were deciphered from the heating runs of DTA experiments. Coexisting phases in the solid state were established from the XRD characterisation of long term equilibrated samples. Preliminary results indicated that the LiCl-

KCl-GdCl3 ternary phase diagram consists of several quasi-ternary sections. The ternary eutectic temperature was observed at 315 ± 3°C in the LiCl-KCl-K3GdCl6 quasi-ternary section, at 308 ± 1°C in the LiCl-K3GdCl6-K2GdCl5 pseudo-ternary section, at 356 ± 4°C in the LiCl-K2GdCl5-KGd2Cl7 pseudo-ternary section and at 366 ± 5°C in the LiCl-KGd2Cl7-GdCl3 quasi-ternary section.

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Thermodynamic properties of ionic liquids containing N-butyl-4methylpyridine tetrafluoroborate in different aqueous biphasic systems

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In this study, liquid-liquid equilibrium (LLE) data of $[BPy]BF_4$ + $CH_3(CH_2)_3OH$ or $CH_3CH(CH_3)CH_2OH$ + H_2O aqueous biphasic systems (ABS) were determined at 97.00 kPa and 303.15, 308.15, 313.15 and 323.15 K. The phase diagrams were drawn to study the phase behavior and binodal curves data were correlated by several empirical equations to verify the accuracy of the data. Meanwhile, the accuracy of tie lines data was also verified by Bancroft and Othmer-Tobias equations. The activity coefficient NRTL model was used to fit the data and the root means standard deviation (RMSD) value were calculated to evaluate the fitting effect. The phase separation ability of $CH_3(CH_2)_3OH$ and $CH_3CH(CH_3)CH_2OH$ at different temperature are discussed. For the studied aqueous biphasic system, the effect of temperature on the separation ability of the phase isn't significant. This paper can be used in the extraction and separation of the aqueous biphasic system, and provide liquid-liquid equilibrium data for recycling ionic liquids.

Nanostructure and solvation properties of several protic ionic liquids

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Keywords: thermodynamics, solvation, ionic liquids, nanostructure

In the last two decades, a huge attention was paid to the studies of solvation properties of ionic liquids, which are important for the prospective applications of these solvents in industrial separation processes. However, only solvation in aprotic ionic liquids (AILs) has been extensively studied. In contrast, almost no data are present on the activity coefficients, solubilities, or enthalpies of solution in protic ionic liquids (PILs) such as alkylammonium salts.

The presence of a network of hydrogen bonds in molecular solvents always leads to a decrease in solubility and an increase in the activity coefficients of low-polar compounds. Thus, one could suggest that hydrocarbons should have significantly higher activity coefficients in PILs than in AILs. However, in our recent work [1], the opposite tendency has been observed.

The limiting activity coefficients of hydrocarbons in alkylammonium nitrates were found to be significantly lower in these PILs than could be expected for the AILs with similar molar volume magnitudes. The effect of increased solubility of hydrocarbons in alkylammonium nitrates can be explained by the peculiarities of the nanostructure of these liquids, namely the presence of polar and apolar domains. The solvation occurs predominantly in apolar domains, which causes a decrease in the activity coefficients and an increase in solubility of hydrocarbons.

At the same time, there are nanohomogeneous liquids among PILs that do not have a domain structure. An example is 2-hydroxyethylammonium nitrate [2]. Its cation has an additional OH-group in comparison with that of ethylammonium nitrate, which drastically changes its hydrogen bonding pattern.

In order to analyse the influence of solvent nanostructure on its solvation properties, we have determined the activity coefficients of hydrocarbons and alcohols in 2-hydroxyethylammonium nitrate as well as butylammonium thiocyanate. According to the neutron diffraction studies, the latter has a domain nanostructure similarly to alkylammonium nitrates. The activity coefficients and Gibbs free energies of solvation of hydrocarbons were much higher in 2-hydroxyethylammonium nitrate than in ethylammonium nitrate, while in butylammonium thiocyanate and butylammonium nitrate these quantities had similar values.

Our molecular dynamics simulations of cavity formation process in considered solvents confirm much higher Gibbs free energy cost of cavity creation in 2-hydroxyethylammonium nitrate than in ethylammonium nitrate. It is also shown that in solvents with domain nanostructure the cavities form predominantly in apolar domain, which explains the observed difference. It can be concluded that the nanostructure governs the solvation properties of PILs. Another interesting consequence is that one can judge about the nanostructure of PILs from relatively simple thermodynamic experiments.

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Thermal and spectroscopical analysis of iron(II) and copper(II) complexes with azomethines

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Keywords: azomethines, transition metal complexes, thermo-gravimetric study, spectroscopic study, biological activity

The roles of biologically active transition metal (such as Fe, Cu) complexes with antibacterial, antifungal, and anticancer property have attracted much interest during last decades. Numerous chelates containing Cu2+ have been shown to possess anti-inflammatory activity [1]. Efforts are now focused to develop novel antitumor drugs which can improve clinical effectiveness, in order to reduce general toxicity and to broaden the spectrum of activity. Due to its interaction with many biomolecules and synthetic substances including organometallic compounds and metal complexes, DNA is a main target for the therapeutic treatment of various disorders and diseases [2]. Metal complex based functional metalloenzymes play also an important role as highly active and selective catalysts governing vital functions of living organisms [3].

In our research project new Fe(II) and Cu(II) complexes were synthesized from the reaction between azomethine derivatives (glyoximes, Schiff bases, semi- and thiosemicarbazones) and Fe(II) or Cu(II) salts, respectively, in suitable solvent. After presenting a short historical survey, classification, and possible application fields of these compounds, we report the study of their thermoanalytical behaviour (TG, DTA, DTG), spectroscopic features (such as FTIR, NMR, UV-VIS, Raman, Mössbauer, ESR spectroscopy, mass spectrometry) as well as their powder XRD. The biological activity of complexes, especially their antibacterial activity, will also be discussed. A few representative examples for their thermal decomposition are shown in Figure 1.

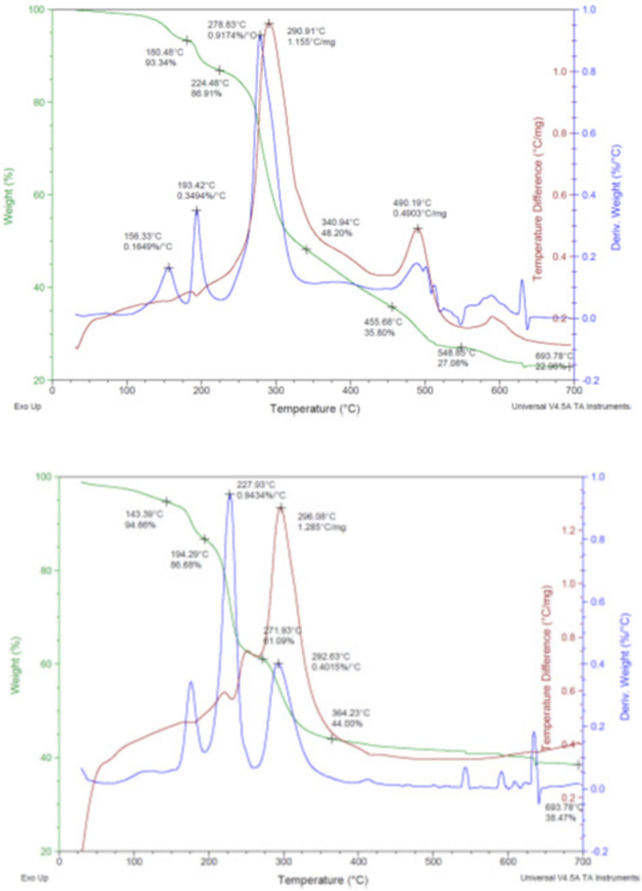

Fig. 1. Thermal decomposition of [Fe(Diethyl-Glyox)$_3$(BOH)$_2$] and [Cu(Et-Pr-GlyoxH)$_2$(2-aminopyrimidine)$_2$].

Acknowledgements

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Poster Presentations

Bio sciences, including food, soil, textile, wood

Glycerol-Starch hydrogel synthetized by Microwave to improve curcumin solubility in water

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Keywords: Microwave, Solubility, Natural dye, Green Chemistry

Curcumin is a natural yellow dye found in the rhizomes of Curcuma longa, which is non-toxic to human health. It has widely been used in medical applications, due to its bactericidal and healing activities [1,2]. However, it is insoluble in water, which spoil its applications in medical field [3]. Taking it in mind, it is necessary new researches to improve curcumin solubility, then this work has synthetized a new glycerol-starch hydrogel (GSH) by microwave irradiation with curcumin (GSCH). Furthermore, the hydrogel is totally soluble in water, solubilizing the curcumin. In Figure 1-a are shown the TG/DTG-DTA of GSH, the hydrogel is stable up to 170.0 ºC and decomposes in a complex way as observed in DTG curve; the mass loss before 170.0 ºC is associated to glycerol evaporation. The Figure 1-b shows the TG/DTG-DTA curve for GSCH, it is observed the same TG curve profile as observed to GSH. The Figure 1-c and 1-d exhibited the DSC curves for GSH and GSCH, both are very similar, in the first heating were just observed a thermal event (endothermic) at 150ºC (GSH) and 135ºC (GSCH) related to glycerol evaporation, in the cooling stage and second heating were not observed any thermal event in both systems.

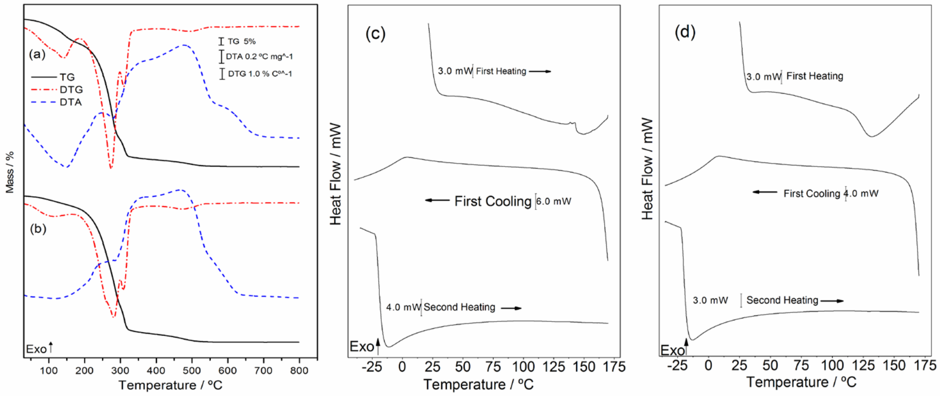

Figure 1. TG/DTG-DTA curves for GSH (a) and GSCH (b). **DSC** curves for GSH (c) and GSCH (d).

Acknowledgments

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Physicochemical properties of native and waxy maize starches under heat-moisture and organic acids treatments

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Keywords: Starch modification, thermal characterization, waxy maize, organic acids.

Starch is widely used in food systems, act as thickening agents, stabilizers and gelling agents, which contributes to the texture, viscosity, mouth feel and shelf life of the finished products or in their manufacturing processes. Modified starch tends to produce a variety of derivatives with altered physicochemical properties and alters structural attributes related to digestibility. In this study, waxy and native maize starch samples were modified by heat-moisture treatment (HMT) in an autoclave. The effect combined with the addition of water and organic acids (acetic, lactic and citric) was investigated in order to understand the influence of these modifications on the thermal, pasting and structural properties. Through X-Ray Diffraction (XRD), it was observed HMT combined with acids did not modify the diffraction pattern of starch granules. Presence of acids led to a viscosity reduction observed by pasting properties (RVA) [1]. Waxy starch samples with organic acids showed a reduction on gelatinization enthalpy (ΔH_{gel}) observed by Differential Scanning Calorimetry (DSC) curves. On the other hand, most of acids combined with native starch did not present ΔH_{gel} alterations. However, lactic acid showed endotherm energy of 8.5 J g^{-1} compared to 7.4 J g^{-1} of untreated sample. As described in the literature, HMT is connected to the emerging concept of 'green chemistry' for environmentally friendly applications and addition of organic acids may contribute to the increase of the resistant starch content [3].

Acknowledgments

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Thermal, structural and mechanical properties of fiber reinforced biodegradable films using different methods of starch extraction

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Keywords: biodegradable films, acid extraction, alkaline extraction, aqueous extraction, casting

The development of biodegradable packaging has been studied to replace synthetic polymers in an attempt to reduce the environmental impact of this material. Starch, abundant material found in several botanical sources and low-cost appears as a potential option for the production of alternative materials for these purposes; mainly in food applications. Thus, the objective of this work was to characterize cassava fiber and avocado seed starch extracted by three different methods: aqueous, alkaline and acid. Thermal, structural and mechanical characterization of the biodegradable films with different proportions of the raw materials was investigated. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis demonstrated that the chemical extraction methods used for the starch did not alter the crystalline structure of the granule, as reported in other study [1]. The different types of extraction influenced the enthalpy of gelatinization of the starch, where the alkaline extraction increased the enthalpy from 7.7 J g-1 to 12.0 J g-1. Thermogravimetry (TGA) showed that the degradation of the films occurred in similar sequential stages due to the evaporation of the free water, volatilization of the water and glycerol mixture and finally the decomposition of the main components starch and fiber respectively [2]. The second mass loss occurred in the range of 115 to 274 ºC, it was observed that the samples containing fibers presented higher degradation temperatures, indicating better thermal stability. In general, the films that were obtained by the starch extracted under acidic conditions presented the most satisfactory results: low moisture content and better mechanical resistance of 3.12 ± 0.35 N mm-2.

Acknowledgments

The authors would like to thank CAPES, CNPq, Fundação Araucária and Paraná State Government for financial support and C-LABMU (UEPG) for XRD and SEM analysis.

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Evaluation of affinity of isoflavones from fermented Chickpea & Red clover sprouts to actin BY isothermal titration calorimetry

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Keywords: isoflavones, fermented sprouts, actin, ITC

Actin is a multifunctional protein that controls most cell processes and functions. It occurs as a main protein in the human body and participates in forming filaments (F-actin) leading to the phenomenon of cell migration in tissue organisms, what contributes to intensity in cancer cell movement and tumour invasion. As we have researched earlier, legume sprouts containing nutraceuticals such as isoflavones have potential of binding to actin and limiting actin polymerization, according to Budryn at al. (2018). However, consumption of sprouts in the raw form carries a risk of poisoning with microbiologically contaminated food, therefore looking for solution to reduce the risk of growth of pathogenic microflora is of great scientific and industrial interest. We used lactic acid fermentation which allowed to increase the content of isoflavones and to reduce of pathogenic microflora count.

The research hypothesis was tested on sprouts of chickpea (Cicer arietinum) and red clover (Trifolium pratense L.), which were cultivated under different types of light: UVA, UVB, white, blue and red, from 3 to 11 days at 18 or 25 ^{o}C and relative humidity of 80%. The samples of sprouts were fermented by lactic acid bacteria and analysed for the profile of isoflavones using the LC-ESI-MS technique. The reaction of binding of isoflavones to actin was evaluated by isothermal titration calorimetry (ITC).

The analysis showed that the richest source of isoflavones were chickpea sprouts after cultivation under blue light at 18 ^{o}C for 10 days followed by 4 days of lactic acid fermentation, which contained 3.81 g of isoflavones in 100 g of dry mass and red clover sprouts cultivated for 11 days under UVB at 18 ^{o}C and fermented 2 days (5.5 g/100 g of dry mass). The fermentation step contributed to the reduction of pathogenic bacteria (by ~3 log CFU/g.).

The ITC study showed that the highest affinity for actin and the highest stability was demonstrated by the fermented chickpea sprouts cultivated for 8 day under white light (ΔG= –28.72 kJ/mol; ΔH= –36.17 kJ/mol) and red clover sprouts cultivated for 3 day under UVA light (ΔG= –28.93 kJ/mol; ΔH= –36.30 kJ/mol) and 10 day under UVB light (ΔG= –28.89 kJ/mol; ΔH= –36.29 kJ/mol). The study showed that fermentation with lactic acid bacteria increased the content of isoflavones, which act as ligands limiting actin polymerization, thus preventing cancer cell movement and cancer invasion.

The study is included in patent application No P.426316

Acknowledgments

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Effect of two types of initiators on the thermal properties of unsaturated polyester resins

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Keywords: unsaturated polyester resins, differential scanning calorimetry, thermogravimetric analysis

During the last years, unsaturated polyester resins (UPRs) have attracted the attention of both academia and chemical industry, since they exhibit great properties along with their controllable and inexpensive production and their innumerable fields of application [1,2]. UPRs are obtained from radical polymerization of unsaturated polyesters with unsaturated monomers which act as crosslinking agents. They also contain initiators, accelerators which promote the curing process, etc. Thus, both the manufacturing and the processing of unsaturated polyester resins evolve various types of chemical reactions, leading to a great versatility of industrial applications and to the urge of fast progress of respective research.

The cross-linking process is a crucial stage of the UPRs synthesis, since during that procedure the initial resins create three-dimensional networks structure and they are transformed into solids. Several types of initiator systems are applied in order to induce cross-linking, with the thermal homolytic dissociation of initiators being the most widely used mode in order to generate radicals for the initiation of the polymerization - the most widely initiator being benzoyl peroxides (BPO) which acts at elevated temperatures. There is, also, another category of initiators, those which induce curing at room temperature - such as methyl ethyl ketone peroxide (MEKP).

In present study, the effect of two different types of initiator systems (BPO and MEKP) were studied on the curing process of unsaturated polyester resins and on the thermal stability of the corresponding cured materials. The studied resins were based on succinic acid, they were cross-linked with acrylic acid and Cobalt (II) ethylhexanoate was used as accelerator. Techniques evolved in the study of thermal properties of studied UPRs were Differential Scanning Calorimetry (both in dynamic and isothermal mode) and Thermogravimetric Analysis (in dynamic mode).

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Evaluation of antidiabetic effects of bioactive isolates from various coffee extracts through binding with PPAR-y

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Keywords: diabetes type 2, PPAR-γ, coffee, ITC

Type 2 diabetes is one of the major metabolic diseases. It is influenced by many factors, mainly malfunctions of the nuclear peroxisome proliferator-activated receptors gamma (PPAR-γ), resulting in disruption of gene expression involved in carbohydrate metabolism, which causes lowering the level of membrane receptor sensitivity for insulin, making it difficult to maintenance glucose homeostasis.

Bioactive compounds contained in coffee can be an example of natural substances of low toxicity, binding and activating PPAR-γ. The bioactive compounds in coffee include antioxidants, mainly polyphenols. We tested coffee bean extracts of two species Arabica and Robusta, green and roasted to light and dark levels and their fractions containing various groups of polyphenols obtained by counter current partition chromatography.

The aim of the research was to evaluate the degree of PPAR-γ activity by bioactive isolates from various coffee extracts of green, light and dark roasted Robusta and Arabica coffees. The calorimetric titration (ITC) of PPAR-γ solution with bioactive isolates from various coffee extracts of green to assess the antidiabetic effect.

ITC analysis of coffee extracts and their fractions showed strong energetic effects of interaction with the receptor of green Robusta and Arabica beans infusions. Among individual bioactive compounds caffeine contained in green Arabica coffee showed the highest affinity ΔG for PPAR-γ of −37.18 kJ/mol and binding constant of 1,83 L/mol but showed low enthalpy of the complex formation (ΔH −2.39 kJ/mol). The less energy needed to form a stable complex (ΔH −8.71 kJ/mol) was observed for the fraction of dichlorogenic acids from green Robusta, with affinity ΔG at the level of −33.70 kJ/mol and binding constant 0,48 L/mol. Studies have shown that coffee extracts are potential PPAR-γ agonists and can be considered as compounds that increase insulin sensitivity.

Acknowledgments

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Combustion calorimetry and its use in stress physiology of plants

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Keywords: combustion calorimetry, abiotic stress, biotic stress , plants

Combustion calorimetry as a commonly used method in thermodynamics has a wide use in the area of evaluating the properties of biological materials and the metabolic processes of plants. There is a mutual interaction between sink and source that influences the creation of assimilate substances, the chemical composition of produced matter, their mutual ratio and storage. Combustion calorimetry monitors and describes this mechanism very well. Additionally, it is a relatively simple and economic method. Using combustion calorimetry, it is possible to gain an overview of the accumulation and translocation of energy matter in the level of the plant, its vegetative growth or ecosystem over the course of the entire ontogenetic development of the plant. This method can be used as a detection method for establishing changes in metabolism and degree of resistance in plants, as well as ecosystems under the impact of biotic and abiotic stress factors, too. The subject of stressor-impact on the content of energy in plant biomass is very complicated because, under natural conditions, stressors do not usually affect the plants individually, but in mutual combination. In the case of biotic stressors, there are two or more living organisms in interaction, mutually influencing their metabolic processes. The content of energy of a host organism after attack by a pathogen (for example the stem rust), is usually higher than in the case of a 'healthy' plant. The infection caused by the pathogenic organism influences photosynthesis and respiration that leads to a change of the source and sink relation. In leaves of Triticum aestivum, infected with powdery mildew, there was an increase in triose phosphate, fructose -1,6-bisphosphate, hexose phosphate, sucrose, fructose and glucose, while to the contrary, phosphoglyceric acid decreased. For example, in barley plants infected with powdery mildew, increased calorific values on infected plant organs 1.4 kJ.g-1 (12.6%) to 12.5 kJ.g-1 DM. While in plant leaves unaffected the calorific value of 11.1 kJ.g-1 DM. Increasing the calorific value on infected plant organs it is affected by the movement of carbon in the affected skin tone and between infected and healthy plants of mesh. Furthermore, there is in infected plants to increase the total amount of carbohydrates and their ratio and their metabolism. In plants growing under conditions of abiotic stressors, there is usually a decrease of energy-rich matter in the biomass of all plant organs. Water deficit is a significant abiotic stressor, causing reduced energy content in individual organs. The water deficit influences the photosynthetic parameters of juvenile corn plants and thus the accumulation of energy into the individual plant organs. For example, in maize plants experiencing drought due to a reduction in calorific value of the rotor, in stressed plants was in the amount of combustion heat 12.94 kJ.g-1 for control plants 13.14 kJ.g-1. The energy content of the above-ground organs was lower by 0.14 kJ.g-1 (1.06%) compared to plants from control conditions (13.21 kJ.g-1) for stressed plants. Changes in energy content were also detected in raspberry in damaged and undamaged spruce forest ecosystems of Slovakia. The average energy content of raspberry damaged ecosystems was 19.13 kJ.g-1 and intact spruce forest was 19.08 kJ.g-1. From this it is therefore evident that the energy content is higher in plants of degraded ecosystems spruce compared with undisturbed ecosystems. The above changes are due to the fact that in certain localities of the Middle Spis was once spirited mining activity. Also in the case of combinations of stress factors leads to a significant decrease in the calorific value of biomass of plant.

Combustion calorimetry has a wide use in the field of the evaluation of the properties of biological materials and metabolic processes of plants. There is a mutual interaction between sink and source that influences the creation of assimilate substances, their chemical composition, their mutual ratio and storage. This method can be used as a detection method for determining changes in metabolism and degree of resistance in plants as well as ecosystems under the influence of biotic and abiotic stress factors.

Acknowledgments

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Dependence of starch gelatinization on heating rate

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Keywords: starch gelatinization, heating rate, fast-scan chip-calorimeter

Gelatinization of starch is the dissolution process via the breakage of intermolecular hydrogen-bonding in the crystalline region. Water molecules enter into the microcrystalline bundle structure, resulting in a decrease in the crystallinity of starch, which is closely related to the food cooking. Starch gelatinization is affected by water content, pressure, particle size, heating rate and other factors. We combined conventional DSC and fast-scan chip-calorimeter Flash DSC1 to heat the starch sample, which has been adequately equilibrated with excess water, in order to observe the characteristics of starch gelatinization in a large scale of heating rates. The thermal contact between sample and chip sensor, the water loss and the necessary pressure during reaction have been taken care. We analyzed the heating rate dependence of gelatinization peak shape, peak temperature and enthalpy. The results are of great practical meaning to the effect of heating rate on the gelatinization kinetics and the critical heating rate to suppress starch gelatinization during heating.

Acknowledgments

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Thermal behavior of some food antioxidants

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Keywords: thermal analysis, antioxidants, differential scanning calorimetry, thermogravimetry

Food additives are added to food products in order to promote enhancement of flavour, appearance and preservation, for example. However, during processing these compounds can be submitted to heating/cooling, thus, it is important to understanding their thermal behaviour in order to define physical transformation, stability and even characterizing the decomposition products. Thus, it is important to develop detailed studies regarding the thermal behaviour of such additives in an extended temperature range from sub-ambient up to degradation. Our group has presented some in investigation in this scope [1,2,3]. In this work a complete study of thermal behaviour of butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tert butylhydroquinone (TBHQ) is presented. Thermal behaviour was elucidated by thermogravimetry (TG), Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and hot-stage microscopy (HSM). Phase changes were elucidated by XRD. TG/DTG curves (in air) of BHA present mass loss in a single step between 85.8–189.4 °C resulting in a 0.19% residue. Similar to BHA, BHT and TBHQ decompose in a single step between 80.5–183.3 and 134.2 and 222.3 °C, respectively, practically without residue. From the DTA curves, melting and evaporation are observed to BHT and TBHQ. For BHA, an endothermic peak at 41.9 °C could be observed, before the melting, referent to a solid-solid transition. Similar to the decomposition in air, it can be observed the same single step for all antioxidant in nitrogen atmosphere, as well as the solid-solid transition for BHA. Phase transitions were studied by heat–cool–heat DSC curves for BHA, BHT and TBHQ in temperatures preceding evaporation. Respective entropy changes were calculated based on peak temperature and enthalpy (ΔH) [4]. For BHA, in the first heating, an endothermic peak at 45.3 °C was observed and attributed to the phase transition (onset temperature 42.0 °C; $\Delta H = +6.4$ J g-1) before the melting at 62.2 °C (onset temperature 57.2 °C; $\Delta H = +75.8$ J g-1). On cooling, no peak was observed. In the second heating, an exothermic peak at 33.9 °C was observed and attributed to the crystallization (onset temperature 28.0 °C; $\Delta H = -75.8$ J g-1) before the new melting at 55.7 °C (onset temperature 50.6 °C; $\Delta H = +73.6$ J g-1). For BHT, only the melting was observed in the first heating at 71.8 °C (onset temperature 69.9 °C; $\Delta H = +94.9$ J g-1), without peak in cooling. An exothermic peak referent to crystallization at 5.91 °C (onset temperature 2.93°C; $\Delta H = -54.1$ J g-1) was found followed by a new melting peak at 60.5 °C (onset temperature 58.6 °C; $\Delta H = +97.0$ J g-1). For TBHQ, similar to BHT, only the melting was observed in the first heating at 130.3 °C (onset temperature 128.3 °C; $\Delta H = +162.4$ J g-1), without peak in cooling, with two exothermic peaks referent to crystallization at 46.7 °C (onset temperature of 40.8 °C; $\Delta H = -52.2$ J g-1) and at 69.2 °C (onset temperature 59.0 °C; $\Delta H = -10.8$ J g-1) followed by a new melting peak at 111.8 °C (onset temperature 109.0 °C; ΔH = +120.3 J g-1). The solid-solid transitions in BHA were also investigated using HSM and XRD. Results corroborated the DSC observations, and confirmed that there is a solid-solid transformation before melting in the first and second heating. Thus, it was possible to elucidate the thermal behaviour of some antioxidants and proposing some phase transitions induced by heating.

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Glass transition temperature of deep-fried food characterized by thermomechanical analysis

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Keywords: glass transition temperature, deep-fried food, water sorption, texture, thermal rheological analysis

Dry starchy food products are commonly glassy solid. Glassy porous structure is the most important factor affecting their brittle texture. When glass transition (glass to rubber transition) is induced by water sorption in the food products, the brittle texture turns into ductile one. In order to control and predict the spontaneous texture change, it is important to understand the glass transition temperature (Tg) of glassy food products. Although differential scanning calorimetry (DSC) is extensively used for the determination of Tg of amorphous solids, study on the Tg of high-fat food products has been highly limited because of a continuous thermal response due to the melting of fat. Thermomechanical approaches, on the other hand, are more effective. Thermal rheological analysis (TRA), which was principally equivalent to thermal mechanical analysis (TMA), was conducted in our previous study, and the Tg of cookies [1] and hazelnuts [2] was evaluated. There has been no clear Tg information for deep-fried food, because deep-fried food has a large amount of oil, making studies more challenging. This study employed deep-fried models (bits of deep-fried tempura batter) and evaluated the effect of water content on Tg using TRA [3]. In addition, effect of glass transition on the texture properties was investigated.

Pellet (compressed powder) and bulk (porous) samples were employed in the TRA measurement. Water content or water activity of the samples was adjusted under various relative humidity conditions at 25 ºC. The samples were compressed at 80 N for 1 min, and then heat-scanned at 3 ºC/min in the temperature range between 10 and 80 ºC. Mechanical Tg was determined form the onset point of force drop. For comparison, DSC measurement was also carried out. In order to confirm the glass transition of the samples, the isothermal mechanical relaxation measurement was carried out. The sample was compressed at 80 N for 3 min. The force-difference (ΔF) between initial force and the force after 3 min was evaluated. The fracture properties of the samples were evaluated using a texture meter. The sample (one piece) was compressed with a plate plunger at 0.5 mm/s. Total number of fractural peaks and first fractural energy were evaluated.

DSC curve showed a complicated thermal response, and thus it was difficult to determine the Tg from the DSC measurement alone. Although TRA measurement for pellet samples showed an unclear glass transition, the measurements for bulk samples showed a large force-drop induced by glass transition. The mechanical Tg decreased with increase in water content because of the water plasticizing effect. From the result, critical water content and critical water activity were determined as the water content and water activity at Tg = 25 ºC. In the isothermal mechanical relaxation behaviour, the ΔF values were almost constant in lower critical water content or critical water activity condition, but began to increase at the higher water content or water activity because of glass transition induced by water sorption. Critical water content or critical water activity decreased with increase in oil content. This suggests that not only water, but also oil play the role of plasticizer to deep-fried food. From the texture study, it was confirmed that the fracture property of the samples changed from brittle to ductile at the critical water content or critical water activity. In order to prevent the texture change of deep-dried food induced by water sorption as long as possible, it is important to reduce the plasticizers such as water and oil.

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Freeze-concentrated glass-like transition temperature of carbohydrate-phosphate buffered saline systems

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Keywords: freeze-concentrated glass-like transition temperature, structural collapse, trehalose, freeze-dry, DSC

Freeze-drying is a widely used drying technique for the stabilization of thermally unstable biomaterials. Some biomaterials, however, experience structural collapse during freeze-drying. Structural collapse occurs when the sample temperature becomes higher than freeze-concentrated glass-like transition temperature (Tg') during freeze-drying. In order to prevent structural collapse, it is essentially important to understand the Tg' of biomaterials. Carbohydrate materials are effective protectants for freeze-dried lactic acid bacteria, but structural collapse occurs readily during freeze-drying. As the reason, it was suggested that phosphate buffered saline (PBS), which was an essential salts for the preparation of lactic acid bacteria, reduced the Tg' of carbohydrates. The purpose of this study was to understand effect of PBS on the Tg' of carbohydrate materials.

Carbohydrate-PBS mixture aqueous systems were prepared at various ratios. Freeze-concentrated glass transition behaviour of the samples was investigated using a differential scanning calorimetry (DSC).

The DSC curves showed two endothermic shifts, a minor endothermic shift at low temperature and a subsequent major one. Although the origins of the two endothermic shifts have been discussed extensively, they are not fully understood [1, 2]. It is known that the major endothermic shift observed at a high temperature is more important for the control of structural collapse [3]. In this paper, the high-temperature endothermic shift was determined to be Tg'. The Tg' decrease with increase in PBS content. To characterize the Tg'-depression behaviour, the Gordon–Taylor was applied. This approach is an empirical expression, but practically useful for the prediction of structural collapse of lactic acid bacteria during freeze-drying.

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Study of the pyrolytic characteristicS of meat and bone meal

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Keywords: meat and bone meal, pyrolysis, thermal analysis

Animal bone char is a natural macro-porous organic phosphorus fertilizer, with a slow release of nutrients. It is produced from meat and bone meal with pyrolysis, controlled thermal decomposition in the absence of oxygen. Meat and bone meal is a product of processing of animal remains, the bulk of which come from slaughterhouses, where they are ground up, heated up with steam for sterilization, and ultimately have animal fats squeezed out to obtain meat and bone meal. Although the content of substances in meat and bone meal depends on individual samples, the meal in general contains about 50% of proteins, 35% of inorganic substances, 8−12% of fats and 4−7% of moisture. It also contains plant nutrients of approximately 8% N, 6% P and 0.5% K. Together with other mineral substances, it contains 11−15% Ca, 0.19−0.25% Mg and 0.2−0.4% S [1]. Phosphorus in meat and bone meal is mostly present in the form of hydroxyapatite (Ca10(PO4)6(OH)2). Low concentrations of organic pollutants (PCDD, PCDF) in remains after pyrolysis of meat and bone meal, as heat treatment destroys almost all persistent pollutants present in the meal, and low concentrations of potentially toxic elements make pyrolytic residue, i.e. animal bone char, a safe and an environmentally acceptable material, with a wide range of potential applications. Due to its high phosphate content, it can be used as a P-fertilizer, although not as soluble as other commercially available agents, or as a stabilizing agent in the remediation of metal contaminated sites [2]. In our research the pyrolysis of meat and bone meal sample at various conditions was studied to evaluate the effects of the heating rate and the final temperature on the course of pyrolysis and on the physico-chemical properties of the residue. Two different final temperatures of pyrolysis process (600 °C and 1000 °C) and five different heating rates (5 K min−1, 10 K min−1, 20 K min−1, 50 K min−1 and 100 K min−1) were used. To evaluate the repeatability, three replications of each thermal process, at same conditions, were performed. After the dehydration of the meat and bone meal sample, the rapid thermal decomposition of the sample near 150 °C began. The temperature, at which the maximum rate of decomposition (inflection point) was observed, was dependent on the heating rate. The shift in temperatures of the maximum rate of decomposition from 309 °C at a heating rate of 5 K min−1 to 361 °C at a heating rate of 100 K min−1 was observed. The mass loss of samples pyrolysed up to 600 °C ranged from 61.2 % to 65.1%, with relative standard deviations of replicates between 0.76% and 1.77%. Although there are statistically significant differences in the mass loss in samples with different heating rates, weak correlation between heating rates and mass loss was observed. The thermal decomposition of meat and bone meal sample mostly ended at 600 °C. A small additional mass loss, which extends to 1000 °C, can be attributed to the thermal decomposition of carbonates and other mineral components present. The average mass loss at decomposition of meat and bone meal sample up to 1000 °C at different heating rates ranged from 61.2% to 67.5%, with relative standard deviations from 0.75% to 9.69%. No statistically significant differences were observed in the mass loss of samples with different heating rates.

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Investigation of side effects in polyneuropathy by DSC caused by cyclophosphamide treatment

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Keywords: popyneuropathy, cyclophosphamide, blood plasma and red cells, DSC

Polyneuropathy is defined as a simultaneous malfunction of several peripheral nerves, which could be a side effect of cancer therapy as well. Well-known, that polyneuropathy is caused by chemotherapeutic drugs in patients with malignant tumor. Many kinds of drugs supposedly cyclophosphamide also can induce a disease classified as toxic polyneuropathy. Cyclophosphamide is a widely used cytotoxic drug, it can causes polyneuropathy as one of its wide side effect spectrum. Cyclophosphamide importance is shown by the appearance on the most important drugs list published by WHO. In present study we analyze a study on peripheral blood plasma and red blood cells by DSC (differential scanning calorimetry), as an established thermoanalitical method, to follow the possible consequence of drug treatment. We used cyclophosphamide treated in vitro animal model (Guinea pig) with a comparable dosage and time handling of human protocol to show evidences of this drug-induced effects. According to our results, we could show a dose-dependent difference between thermal parameters of untreated and treated samples, which can be detected by DSC. It proved that we can create new possibilities in the detection and prognosis of expected and unwanted side effects of cyclophoshamide such as polyneuropathy.

Effect of extraction methods in oxidative stability and antioxidant potential of Araçá (Psidium cattleianum) seed oil

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Keywords: oil seed extraction, ultrasound, thermal analysis

Araçá (Psidium cattleianum) is a Brazilian native fruit which is naturally distributed in a wide area of the National Territory [1]. Studies are generally conducted with a focus on the nutritional and functional characteristics of fruit pulp. However, as a byproduct of its processing, araçá seeds are an important alternative source of oil, with about of 12% of its composition. The fruit is small but presents a high number of seeds, whose oil contains linoleic acid as a major fatty acid [2] which is not synthesized by the human organism [1]. In order to improve the oil extraction of seeds, it is important to choose methods that provide high efficiency with a low degradation of bioactive compounds. Ultrasound assisted method is known as an alternative technique of vegetable oil extraction which enhance the yield, allow the use of alternative solvents and maintain heat sensitive components, as phenolic compounds [3], whose extraction is also influenced by solvent polarity, phenolic polymerization degree and their interaction with other components of the samples [4]. In this way, the aim of this study was to evaluate the phenolic content, antioxidant activity and oxidative stability of araçá seed oil extracted by two different methods: Bligh and Dyer (BD) [4] and Ultrasound-assisted (US) (Ecosonics, Tecnal Q5.9, frequency: 40KHz; power: 200W) at 34°C for 30 min using hexane as solvent. Thermal analysis (Thermogravimetry and Differential Scanning Calorimetry), Total Phenolic Compounds, DPPH, FRAP and evaluation of oil quality (Peroxide value, Acidity and Conjugated Diene Value) was carried out in the araçá oils. The TG/DTG data showed that the stability temperature is similar for both oils, around 205 °C. The oil decomposition occurred until 590 °C and 575 °C, and there was the formation of a 3,62% and 3,75% of carbonaceous residue, for BD and US respectively. The oil extracted by BD presented onset oxidation temperature – OOT of 171 ºC, while the OTT of the oil obtained by US was 167 ºC. There was no difference between methods considering total phenolic compounds, acidity and conjugated dienes. However, the oil extracted by ultrasound method presented higher antioxidant activity, possibly affected by choice of solvent applied, and higher peroxide value, due to cavitation bubble formation which induces the primary oxidation compounds formation. The oil extracted by US presented better results considering antioxidant potential, although it presented lower OOT and temperatures of thermal degradation, which corroborates with the oil quality results.

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Changes in blood serum thermal behavior during sports training enriched with biological regeneration treatments

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Keywords: differential scanning calorimetry (DSC), exercise, human blood serum, sauna, whole-body cryostimulation

Biological regeneration treatments, such as sauna or cryostimulation are used to help athletes to better support the training workload, to prevent the deleterious effects of strenuous exercise and to improve recovery. A moderate-intensity and sometimes strenuous exercises are an essential part of the training and offer a number of important health benefits. However, such exercises increase the risk of injuries, can weaken the immune system temporarily, increase inflammatory processes and have other adverse effects. Recently, the differential scanning calorimetry (DSC) has been widely applied to the analysis of blood plasma, serum or other biofluids to obtain information on the health status of the person examined. DSC has been found useful in the diagnosis and monitoring of diseases [1-5]. In previous studies we made attempts to show the utility of DSC method in sport medicine [6-8]. The purpose of this study was to evaluate whether heat treatments applied during the exercise session modify athletes' response to effort and recovery period. The thermal profiles of blood serum collected in four stages of each training session: before exercise, after exercise, at 1 hour recovery and after 24 hours of rest were monitored by VP DSC MicroCal instrument between 20–100 ºC with 1 ºC min-1 heating rate. The denaturation characteristics of serum solutions have demonstrated specific changes in various points of exercise session before and after a treatment cycles. DSC could be a useful tool in the detection of the changes in athletes' blood serum in response to exercise and regeneration treatments providing help in effective sports training.

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Edible vegetable oils enriched with carotenoids extracted from the by-products of sea buckthorn (Hippophae rhamnoides ssp. Sinensis). a study of some characteristic properties and the effect on the thermal stability

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Keywords: carotenoids, edible vegetable oils, sea buckthorn, thermal stability

In the recent years, it has been granted a growing interest to the substitution of synthetic food antioxidants by natural ones, while a special attention was directed to their extraction from the by-products of the food industry. Sea buckthorn (Hippophae rhamnoides) by-products are promising sources of bioactive compounds that could be used for their favourable nutritional and functional properties. In this study, ultrasound-assisted extraction on one hand and maceration on the other hand have been used for the direct enrichment of edible oils (extra virgin olive oil, unrefined and refined sunflower oil) with carotenoids from dried sea buckthorn by-products. Total carotenoids content and ABTS free radical scavenger activity of both enriched and commercial oils were determined by spectrophotometric methods, and the colour was evaluated according to the CIELab colour space. The oxidative stability of vegetable oils containing the extracted pigments was assessed in terms of peroxide value, while the thermal stability of the oils was evaluated by thermogravimetry and by differential scanning calorimetry. It was shown that the ultrasound-assisted extraction was more effective than the maceration for the extraction of carotenoids from dried sea buckthorn by-products. ABTS radical scavenging activity has been slightly improved for all the oils studied after carotenoid enrichment, while the oxidative stability increased in extra virgin olive oil but decreased in unrefined and refined sunflower oils. Extraction of sea buckthorn by-products significantly ($P < 0.05$) reduced lightness and increased redness and yellowness of the oils.

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Ultrasonic modification of purple cará starch (Colocasia esculenta B. Tini): morphological, pasting and thermal properties

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Keywords: ultrasonic, purple starch, thermogravimetry, pasting properties, physical modifications.

Physical modifications are performed to change and increase the limiting functionality present in native starches [1-2]. Among them, it has been emphasized the ultrasonic treatment, which has been used due to minimization or even elimination of chemical substances, does not require heat treatment, reduces the effluent production, energy consumption and process time is lower [3-4]. Therefore, this study investigated the effect of ultrasonic treatment on the structural and physicochemical characteristics of purple cará starch. The native starch was extracted by the aqueous milling of the flour (4:1, water: flour, w/w). Then, the suspension was sieved and centrifuged for 15 minutes at 4 °C, after this, was dried in an oven (40 °C, 24h), and kept in a desiccator over anhydrous calcium chloride, for analysis. For modification, native starch suspensions (10% w/v) were prepared and placed in an ice bath, subjected to probe ultrasound (20 kHz) at vibration amplitudes of 40–60%, for 30 min. Ultrasound-treated starches were dried and kept in the same conditions as native starch. Field emission scanning electron microscopy (FEG), pasting properties (RVA), and thermal analysis (Thermogravimetry – TG and Differential Scanning Calorimetry – DSC), was applied to investigate the effect of ultrasonic treatment on the starches. The average obtained for the diameters observed by FEG of the native purple cará starch was 1,96 µm. After modification, a decrease of up to 63.25% in the diameter of the granules was observed. In the thermal decomposition, the dehydration of the samples occurred below 161 ºC, with the maximum loss rate occurring between 122–130 ºC. An increase in thermal stability was achieved after treatment of the starch (up to 268 ° C). Ultrasound did not change the gelatinization transition and enthalpy temperatures of the samples, and no significant difference was observed. An increase in peak and final viscosities, and a reduction in breakage and pulp temperature were observed for the sonicated starches. Thus, the ultrasonic treatment allowed the reduction of the granule diameters, with an increase in its thermal stability, preserving the gelatinization parameters of the starch.

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Dual modification by phosphating and ball-milling in pinhão starch, a study of its thermal, structural and morphological properties

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Keywords: Araucaria angustifolia, thermal analysis, dual modification

The pinhão, *Araucaria angustifolia* seed, has on average 70% starch (dry basis) and presents important nutritional aspects [1,2]. Native starches are not always the most suitable for specific processes, so to obtain necessary characteristics, one or more physical, enzymatic or chemical modifications are performed. They may alter some of its properties, such as: enthalpy, retrogradation, syneresis, swelling, crystal order, among others. Thus, the objective of this study was to evaluate the effect of ball-milling on the properties of the *pinhão* starch in its native and phosphate form. The analysis performed were: thermogravimetry (TG), differential scanning calorimetry (DSC), field emission gun-scanning electron microscopy (FEG-SEM) and X-ray diffractometry (XRD). The *pinhão* starch were phosphated in accordance with Lim and Seib [3]. Native and phosphated starch powders were ground in a vibratory ball mill (MM400) for 30 min [4]. TG curves showed three mass losses, associated with dehydration, macronutrients decomposition and oxidation of organic matter. After grinding of the starches a decrease in thermal stability was observed, especially when doubly modified. More pronounced differences for gelatinisation were observed for the double modified sample, which showed a reduction in To and Tp, an increase in the gelatinisation temperature range. The phosphating caused an increase in the enthalpy of the starch, however, when added to the ball mill, an expressive reduction of the enthalpy was verified. Phosphated *pinhão* starch showed an increase in the degree of relative crystallinity, contrary to the behaviour of the samples subjected to grinding, in which a decrease was observed. The *pinhão* starch presented peaks at 15° and 23° and a doublet at 17 and 18° (2θ), classified as C-type. The diffraction pattern did no change after dual modification. No significant differences were observed for the mean diameter of the granules after the applied modifications, that is, neither the phosphating nor the mill caused variations in the size and shape of the *pinhão* starch granules. The double modification of the *pinhão* starch exerted a more intense alteration in its properties, in relation to the individually applied modifications.

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Thermal, structural and morphological characterisation of organic rice starch after physical treatment

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Keywords: *Oryza sativa L*, thermal analytical techniques, ultrasound

Rice (*Oryza sativa* L.) is a cereal of great economic and nutritional importance due to its expressive consumption. Its contribution in the diet is related to its protein value, but also energetic due to the high content of starch (90% d.b.) [1]. To achieve new properties or improve the characteristics presented by native starch, modifications are carried out, catching the attention of many researchers. Therefore, this study aimed to analyse the effects of ultrasound on the thermal, structural and morphological properties of organic rice starch. The starch was extracted by the aqueous method, followed by alcalase treatment for protein removal [2]. To evaluate the effect of time (15 and 30 min), starch aqueous suspensions concentration (5% and 10%) and amplitude (75% and 100%), the 2^3 factorial design was applied in samples treated by alcalase. The properties of native organic rice starch before and after treatment with alcalase, as well as after the ultrasound treatment were analysed.by thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffractometry (XRD) and field emission gun-scanning electron microscopy (FEG-SEM). The first inflection in the TG curve was related to sample dehydration. Subsequent peaks refer to degradation of the amylose and amylopectin chains, followed by oxidation of the sample. After treatment of the native starch with the alcalase, a reduction in the thermal stability temperature was observed. When physically modified, under greater amplitude of vibration, shorter time and lower concentration, an increase in the thermal stability of the starch was observed. Therefore, the US made possible the increase of the thermal stability of the organic rice starch when greater acoustic cavitation occurred in a more diluted medium, under a short time of exposure. When the starch was treated by alcalase, there was a reduction in the gelatinisation transition temperatures and an increase in the gelatinisation enthalpy (2.5 Jg^{-1} to 3.8 Jg^{-1}). By subjecting these samples to the ultrasound, an increase in T_p was observed and there was no significant difference for enthalpy in most treatments. The concentration influenced the ΔH_{gel} only of the treatments under the lowest amplitude of vibration (75%). XRD revealed the presence and characteristics of the crystalline structure of the starch granules. FEG showed that alcalase treatment was efficient because no proteins were observed in the images. None of the US treatments altered the size and shape of the granules. The use of the physically modified organic rice starch may be an alternative for use as an excipient in the pharmaceutical industry and encapsulating agent in the food industry.

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Thermal characterization of atemoia oil obtained by different methods

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Keywords: *Annona cherimola Mill.* x *Annona squamosa L.*, fatty acids, thermal analysis

The atemoia (*Annona cherimola* Mill. x *Annona squamosa* L.) is an interspecific hybrid between cherimolia (*A. cherimola* Mill.) and fruta-do-conde (*A. squamosa* L.) which grows best in hot climate regions [1]. The pulp of the fruit is very aromatic and sweet, presents slightly acidic characteristic and black seeds [2]. The study of fatty acids from different sources has been the focus of several studies in recent years. The characterization of alternative sources of vegetable oils becomes a very promising field for potential use in the food, pharmaceutical and cosmetic industries [3]. The objective of this study was to apply thermal analysis (Thermogravimetry and Differential Scanning Calorimetry, both at a constant temperature scan rate: 10°C min^{-1}) to evaluate the thermal stability and oxidation onset temperature (OOT) of atemoia seed oil extracted by three different methods: mechanical pressing (without solvent), cold solvent extraction (Bligh & Dyer) and hot solvent extraction (Soxhlet) [4]. The TG curves show that the hot extracted atemoia oil had a higher stability (222°C) followed by the cold extraction (211 °C) and mechanical extraction (200 °C). The degradation temperatures of the samples, corresponding to 3 mass losses, were different for each extraction method. The DSC curve of the mechanically extracted oil showed an oxidation onset temperature of 173 °C. This reaction finished at 210 °C, with ΔH_{oxi} about 560 J g^{-1}. In the established temperature range for DSC analysis (20–350 ºC), the exothermic peak did not concluded at this temperature for atemoia oil extracted by Bligh e Dyer and Soxhlet methodologies. In this way, it was possible to observe only the OOT of these oils, about 270 °C and 233 °C respectively. In accordance with the OOT, the mechanical extraction promoted a lower initial oxidation time of the atemoia oil (14 min). The longer time was obtained for the cold extracted oil (25 min). Therefore, the thermal stability of the atemoia oil as well as the oxidation onset temperature and initial oxidation time varied depending on the extraction method.

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Organic red rice starch: double physical modification

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Keywords: Oryza sativa, thermogravimetry, differential scanning calorimetry, viscosity.

Unconventional starches have aroused the interest of different industries due to their characteristics and the possibility of diversifying their industrial use, highlighting organic red rice in this study. Their properties may be adapted to specific processes from modifications. Among the possibilities, physical treatments, such as Annealing and Heat-Moisture Treatment have gained greater prominence because they are considered clean technologies [1,2]. In addition, they may be applied in organic products. The extraction of organic red rice starch occurred in aqueous solution [3]. With the starch isolated, annealing was performed at a temperature of 50 °C hydration in a ratio of 1:5 (w: v), kept under stirring at 24 and 48 h. Then, the moisture of the samples was equilibrated to 15 and 20% for HMT, which was carried out in an autoclave at 121 ºC for 1 h. The characterisation of the native and modified starches was performed through thermal analysis (thermogravimetry - TG, differential scanning calorimetry – DSC), high resolution electronic microscopy (SEM-FEG) and viscoamylographic analysis (RVA). Three mass losses were observed from TG for all the samples. Double-modified starches showed higher thermal stability (292 ºC) when compared to native starch (265 ºC). The stability temperature was higher for all modified samples, being more pronounced after 48 h of annealing. The double modification did not promote changes in the stability of the samples with each other. The enthalpy of gelatinisation was increased for the doubly modified samples, in relation to the native starch (6.19 Jg-1), except for treatment with HMT at 20% moisture, where there was no significant difference. The pasting behaviour of red rice starch was also influenced by the physical treatments. Annealing at both 24 and 48 h increased the peak viscosity of the samples, as compared to the native one (442 mPa.s), while the double modification decreased the peak viscosity. The shape and size of the granules remained unchanged after the treatments. Thus, the double modification caused changes in the thermal and pasting properties of organic red rice starch.

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The parameters describing the heat flow from maize seeds depends on the amount and composition of microbiota

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Keywords: Bacillus, bacteria, fungi, isothermal calorimetry, Lactobacillus, yeast

The dependence between microbiological contamination of maize seeds (quantity and quality of the microbiota) and the parameters describing heat production by seeds was sought. For this purpose, the heat rate curves versus time (ϕ-t plots) and heat rate values (*Rq*) were analyzed. Maize seeds were introduced into 4 ml sealed stainless steel ampoules and inserted into a calorimeter (TAM III, TA Instruments) with six channels. The calorimeter continuously records the heat rate in µW ($\phi = dQ/dt$) in a result file that can be plotted versus time (ϕ-t plots). The quantitative heat rate is determined by integrating the ϕ-t plots over a time interval of 6 hours to give the heat rate (*Rq*) in mJ per gram of seeds and hour (mJ g^{-1} h^{-1}). After calorimetric measuremants, 100 µg of grinding corn seeds were taken from averaged sample, homogenized with TissueLyser LT and isolated in the QiAmp Fecal kit. The volume of the final working liquid was 100 µl. Real-time polymerase chain reaction was performed using standards cloned into a plasmid (TOPO cloning kit 2.1). The reaction was carried out using a Maxima Probe qPCR Master Mix 2x. Required for the components of microbiome primers, probes and sequences was based on the literature data - total bacteria [1], total fungi [2], yeast [3], *Clostridium* [4], *Penicillium* and *Aspergillus* [5], *Lactobacillus* [6] and *Fusarium* [7]. Amplification was performed in adapted thermal profiles and cycles. The efficiency of qPCR had value between 0.97 to 0.99. It has been shown that in the case of maize seeds less affected by *Bacillus* and fungi, the fi-t curve (in the range of 0-6 hours) has a falling shape, while for more infected it grows almost linearly. The more infected seeds also show significantly higher heat rate values (*Rq*). The described research can be used to quickly assess the degree of seed infection.

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Step by step monitoring of early stages of corn germination via isothermal calorimetry and FT-Raman spectroscopy

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Keywords: seeds germination, FT-Raman analysis, isothermal calorimetry, deconvolution

Thermoanalytical methods are widely used to study various seeds germination process [1-4]. The goal of our study was to monitor the early stages of corn seeds germination. In order to perform the task, the isothermal calorimetry method was used. The metabolic activity of maize seeds was measured at 20 ºC in an isothermal calorimeter TAM III (TA Instruments) equipped with TAM Assistant Software. The dry seeds were placed in measuring ampoules with lids, which enabled air exchange [5]. After one hour stabilization, the rate of heat emission in microwatts (φ = dQ / dt) was recorded for 48h hours. That allowed to plot φ as a function of time (φ-t graphs). The quantitative value of heat emission rates was determined by integration of φ-t graphs to obtain the heat emission rate (Rq) in mJ per gram of seed and per hour (mJ•g-1•h-1). This value was taken as the metabolic activity of the sample. At the same time, photographic documentation of germinated seeds was carried out in order to correlate the heat flow changes with morphological processes.

Along with the calorimetric measurements, in the same time regime, the FT-R measurements were made. It was noted that the activation of the germination process results in the appearance of a very strong signal deriving from proteins, while its intensity, after a rapid increase registered in the 6th hour duration of the experiment, was successively reduced to the 48th hour. This regularity was observed both in the upper and lower part of the embryo. This fact is related to the hydrolysis of maize proteins. The resulting Raman spectra, or rather a fragment depicting the vibrations characteristic of the amide I band, were deconvoluted to illustrate changes in the secondary structure of proteins associated with germination.

The obtained results will be presented and discussed in this work.

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Isothermal calorimetric measurements were performed in the Isothermal Calorimetry Laboratory belonging to The Franciszek Górski Institute of Plant Physiology, Polish Academy of Science, Kraków, Poland

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Application of isothermal calorimetry to assess the quality of humidly maize seeds treated with ozone and H_2O_2

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Keywords: seeds storage, pathogens, fungi, microbiota, metabolic activity

Ozone and hydrogen peroxide are a strong oxidizers that can be used to control the amount of microorganisms as well as for the removal of parasites [1]. In addition, they are more environmentally friendly than traditional plant protection products, pesticides and fungicides [2]. The storage of humidly maize seed (Zea mays L.) intended for the production of bioethanol in silbags causes the seeds to be vulnerable to attack by pathogens, especially mold fungi and yeast. In these studies seeds were treated with ozone and H_2O_2, and the effectiveness of this procedure was determined by means of isothermal calorimetry. It was assumed that the thermal activity of the sample is a resultant of heat production by seeds and microorganisms that colonize them. The measurements were made using an isothermal calorimeter TAM III (TA Instruments, Lindon, UT). The amount of microbiome on the seed surface was analyzed by quantifying the copies of the genes of selected microorganisms (Real-Time PCR). The total amount of bacteria, fungi and yeasts as well as the determination of pH, redox potential and salinity in the samples were determined.

Treatment with ozone and H_2O_2 caused a decrease in the thermal activity of the sample compared to the control and reduced the total amount of bacteria, yeasts and fungi growth. There was an inverse relationship between the amount of lactic acid bacteria and fungi (including yeast).

Based on the collected data, a mathematical model was developed to predict the degree of maize seeds contamination based on physicochemical analysis, including calorimetric analysis. As an indicator of microbial contamination, the amount of DNA (determined in molecular research) derived from seed-associated microbiota was assumed. Into the model introduced variables that characterize the biological material under investigation, such as: heat emission, water content in seeds, pH, redox potential and salinity. The obtained results show that on the basis of simple physicochemical measurements it is possible to predict the level of maize seeds contamination with a probability of about 70%.

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Isothermal calorimetric measurements were performed in the Isothermal Calorimetry Laboratory belonging to The Franciszek Górski Institute of Plant Physiology, Polish Academy of Science, Kraków, Poland

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Study of novel bio-based unsaturated polyester resins based on succinic acid

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Keywords: bio-based unsaturated polyester, succinic acid

Unsaturated polyester resins (UPRs) are one of the most important types of thermoset polymers in industry, due to their excellent mechanical properties, their easy processability, their high resistance to chemicals and foremost their low cost, and therefore they are widely used in construction, marine, automotive and aerospace industry [1,2]. Though, over the last years, chemical industry is facing considerable issues associated with the continuous depletion of fossil fuels and the enormous fluctuations in oil price. Furthermore, environmental issues arise, leading to the increasing public awareness, as well to the constitution of regulations towards the usage of renewable feedstock for products which are chemically manufactured. This shifting from a petroleum-based to a bio-based industry can be achieved by introducing bio-based polymers, reducing the fossil fuel dependency and providing sustainable and viable solutions. The shifting of the production of UPRs from petrochemical-based to bio-based resources has led the scientists to the research of adequate replacements derived from renewable resources. In this work, novel UPRs based on succinic acid were synthesized. Succinic acid is a C4 dicarboxylic acid which finds applications in diverse sectors such as the food, the chemical and the pharmaceutical industry [3]. It constitutes a fully bio-based monomer, since it is produced from renewable feedstock through fermentation. In current study, the obtained resins were studied by means of ^{1}H NMR and FTIR in order to confirm their successful synthesis. Furthermore, DSC was employed in order to examine parameters of the cross-linking reaction, while TGA was used for the investigation of the cross-linked materials' thermal stability.

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Calorimetry

DSC research of the Polystyrene/bentonite composite films

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Keywords: polystyrene/bentonite composites, differential scanning calorimetry, glass transition temperature

Priority area of the modern chemistry and materials science is development of polymeric nanocomposites with controllable properties. Harsh conditions of polymer operation in power engineering and in chemical, petroleum, and pulp-and-paper industries impose stringent requirements upon the properties of the polymers. Effective way to meet these requirements is insertion of fillers into polymer matrix. Such composites may have applications in electronics, biotechnology, medicine, due to their improved mechanical, electrical, thermodynamic, antimicrobial properties [1, 2].

Polystyrene (PS) is well-known film-forming polymer often used for different modifications with low molecular compounds of special properties, including laminar aluminosilicates. Bentonite (Bent) is one of best-known and the most important clay minerals that can be used for intercalation of polymers. In the current study, the samples of the PS/Bent composite films were produced. Also an effect of the filler content on the glass transition temperature of composite was researched.

To preparation of the film composites, atactic polystyrene (Aldrich, US; $M_n=1.4\times10^5$, $M_w/M_n=1.64$) and bentonite (Sigma Aldrich, US) were used. Bentonite particles were immobilized into the polystyrene matrix by mechanical dispersion. For this, PS and PS/Bent solutions in o-xylene were prepared at various mass ratios and stirred using a magnetic stirrer. The films were prepared by casting pure and modified polymer solutions onto a Teflon substrate followed by drying at room temperature until the solvent was completely removed.

Thermal behavior of the film materials prepared was studied using DSC. It was found for all film, when the temperature rises, a break in the thermogram is observed. This break corresponds to the relaxation transition from the glassy state to the highly elastic one. Such dependences are associated with changes in the heat capacity of the material during the relaxation transition. Also it was found that the clay concentration in the film affects the glass transition temperature (Table).

Table. The glass transition temperatures of the polystyrene/bentonite composites

Concentration of bentonite, wt. %	**T_g, ^{0}C**
0.0	70.9
0.1	73.9
0.5	77.7
1.0	79.1
3.0	84.8
5.0	85.7

For unmodified polystyrene, the glass transition temperature is 70.9 °C, whereas the composites have higher T_g values: the introduction of bentonite (5 wt. %) into polystyrene leads to an increase in the glass transition temperature by almost 15 °C. The revealed effect is associated with a decrease in the mobility of polymer chain segments as a result of their interaction with clay. This decrease in the mobility of the segments appears to take place near the clay particles.

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Measurement and prediction of phase diagram of some pharmaceutical substances

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Keywords: Solubility; DSC92, Pharmaceutical; UNIFAC; NRTL; IDEAL

Liquid-Solid equilibria are less measured, relatively to the other two types of phase equilibria vapor and/or liquid phases.

The first aim of this work is to estimate the melting temperature using differential scanning calorimetry (DSC92).

In second stage we are interested in modeling of these phase equilibria by means of various thermodynamic models such as NRTL and UNIFAC which are tested for binary and ternary systems. The ideal solubility is also calculated.

Several systems have been considered to study the solubility of Citric Acid, Mannitol and Menthol in various solvents such as; Water, Formamide, Lactose and Trehalose.

The results of our study and literature, concerning the phase diagrams show a good agreement, particularly for the NRTL model, compared to UNIFAC which is based on the concept of group contribution.

Enthalpies of immersion in caffeine solutions of SBA-15 and amino functionalised SBA-15

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Keywords: Mesoporous silica, immersion calorimetry, emerging contaminants

In recent decades a group of compounds called emerging contaminants (EC) have been detected in different aquatic environments. Caffeine (CFN) is considered an EC, and has been found in various studies on surface water and wastewater around the word. For decontamination of wastewater and water source, the use of porous solids is a potential technique. In this work, mesoporous silica SBA-15 was prepared and modified with 3-aminopropyltriethoxysilane via post-synthetic reaction from SBA-15 to obtain amino-functionalised SBA-15. The structure and physicochemical properties of the materials were determined by nitrogen adsorption–desorption isotherms (Fig 1.), infrared spectroscopy, thermogravimetric analysis and acid-based titration. Immersion enthalpies were determined using a heat conduction calorimeter Calvet type of local construction and were used caffeine solutions at different concentrations like immersion liquids. Calorimetric studies showed that the immersion of the SBA-15 in each solution generated values of enthalpy of 13,90 to 194,06 J g–1 and the immersion of the SBA-15-NH2 in each solution generated values of enthalpy of 7,22 to 60,34 J g–1. The results show that functionalization of SBA-15 produced differences in characteristics of solids, since energy and affinity for the calorimetric liquids are related to the solids surface properties, immersion enthalpy were different.

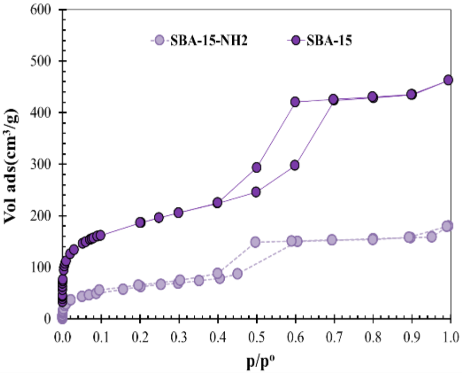

Figure 1. N_2 adsorption-desorption isotherms at –196 °C

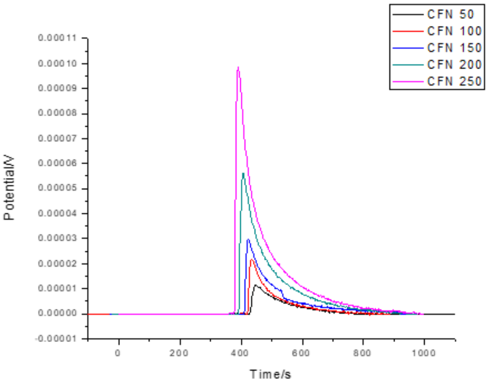

Figure 2. Curve of immersion of caffeine in SBA-15 for SBA-15 and SBA-15-NH_2

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Development and application of a multi-purpose calorimeter with micro bomb combustion–dissolution–reaction

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In this work, a multi-purpose calorimeter with micro bomb combustion-dissolution-reaction was firstly developed based on the SRC-100 precise dissolving-reaction calorimeter. The new calorimeter mainly includes three innovation points: one was to improve the calorimetric vessel, that is to say, the single-layer heat insulation Dewar bottle has been modified into a double-layer heat insulation Duval bottle; Second, the calorimetric vessel (Dewar bottle) was immersed in the thermostatic tank to reduce the influence of indoor air convection on the calorimetric system, and finally a thermal insulation layer and thermal shield were added to the outside of the thermostatic tank. The precision of temperature measurement is ±0.00001 K and the precision of temperature control is (25.000 ±0.001) K. The precision of the instrument is better than 0.05 % in the sample range of 10–30 mg.

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Heat of adsorption: a comparative study between the experimental determination and theoretical models using the system CH_4-MOF´s

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Keywords: adsorption calorimetry adsorption heats, Clausis-Clapeyron, Dubinin-Astakhov, isosteric heats, MOF´s

When the study of an adsorption process is carried out, it is based on the measurement of two properties: the adsorption isotherm and the adsorption heat. The isotherm corresponds to the measure of the adsorption capacity, while the heat of adsorption is a variable that shows the strength of the interactions between the adsorbate and the solid adsorbent. Solid gas adsorption research is commonly used for the characterization of surface properties and in other applications such as the separation and capture of gases and vapors [1,2]. The objective of this work is to compare isothermic heats of adsorption measured by different techniques. The methods that are used most frequently to evaluate it is the determination of the adsorption isotherms covering wide ranges of pressure and temperature, using the so-called isothermal adsorption method. On the other hand, the direct quantitative evaluation of the isosteric heats can be carried out using the calorimetric-coupled volumetric method, which consists of the simultaneous measurement of heat and adsorption. In this work, we compare the isosteric heats of methane adsorption in highly microporous materials measured by both methods. In addition, the experimental data are compared with the isosteric heats obtained using the theoretical-analytical models of adsorption: Dubinin-Astakhov, Tóth and Unilan modified, to establish the reliability and limitations of both methods [3,4]. To achieve the objectives of this research, we measured the isosteric methane heat in five metal structures organic framework (MOF's): MOF-74, ZIF-8, HKUST-1, MOF-5, and MOF-177 using both methods experimental. For all MOFs, we found a good agreement between isosteric heats measured using calorimetric and isosteric methods in almost the entire load range studied. The prediction of the models, on the other hand, show deviations that were associated with the structure of each MOF used and to the methane load. The order of the isosteric heats is consistent with the intensity of the methane interaction fundamentally with the results of the textural analyzes determined for each of the MOFs.

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Calorimetric study of lutetium orthoniobate

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Keywords: DSC, drop calorimetry, phase transition

The LuNbO4 are known to crystallize in a fergusonite-type structure (a monoclinic structure, space group I2/a), undergoing a pure and reversible ferroelastic phase transformation to a scheelite-type structure, with a tetragonal system lattice (space group I4/a), only stable at high temperatures [1].

The present study is aimed at experimental measurement of heat capacity and enthalpy change in the wide temperature range, with special attention to the region of phase transition, and the calculation of the standard thermodynamic functions of LuNbO4.

The low-temperature heat capacity of lutetium orthoniobate was measured by relaxation and adiabatic calorimetry in the range 5-340 K. The experimental data obtained by both methods were joint fitted using an equation that is a linear combination of the Debye and Einshein functions.

In this work we the high-temperature heat capacity of LuNbO4 was studied by differential scanning calorimetry using STA 449 F1 Jupiter® (NETZSCH). Particular attention was paid to the region of phase transformation. The temperature dependence of heat capacity has a slight step-like change around Ttr in the mode of heating and cooling. The phase transition from the monoclinic to tetragonal phase was continuous and showed characteristics of a second order transition. The obtained results were compared with the data of high-temperature XRD and the results of dielectric measurements [2].

Drop calorimetry measurements of high temperature enthalpy increments of LuNbO4 were carried out using a SETARAM high-temperature calorimeter HTC1800K/DSC2000K. Using low-temperature enthalpy change values, the data were reduced to the form Hmo(T/K)–Hmo(0) and were compared with calculated enthalpy changes obtained from DSC measurements.

A complex study of thermodynamic properties by various methods in the same temperature range made it possible to obtain more reliable values of the heat capacity and to thoroughly describe the observed anomalies.

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Calorimetric investigation of mixed feed substrate feeding for recombiant pichiapastoris expressing human interferon alpha2b

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Keywords: Pichia Pastoris, Interferon α 2b, Mixed Feed, Calorimeter

Recombinant protein production in *Pichia pastoris* is usually based on alcohol oxidase promoters (AOX1 and AOX2) which are regulated by methanol. Methanol feeding poses challenges in fermentation process, which includes temperature control (due to high metabolic heat rates), high oxygen demand and toxicity of cultures due to its over feeding. In this study, the influence of mixed substrate feed on the growth of a *P.pastoris* strain expressing a recombinant protein Interferon α 2b was investigated in a heat compensation calorimeter. Three different feed combinations i.e, methanol as a sole carbon source, methanol + sorbitol and methanol + glycerol were used in *P. Pastoris* fermentation towards expression of huIFNα2b. Mixed feed ratio of 0.8 C-mole methanol and 0.2 C-mole sorbitol, 1.0 C-mole methanol and 0.1 C-mole glycerol were found to be optimal for enhanced huIFNα2bexpression. Real-time thermogram deciphered the metabolic shifts related to dual substrate uptake, corroborated with respirogram and off-line measurments. A significant drop in metabolic heat production in induction phase in mixed feed regimes of methanol/sorbitol (55 %) and methanol/glycerol (39%) was observed relative to the fermentation with methanol as sole carbon source. The drop in metabolic heat rate suggests that the carbon flux channelling to the anabolic activity is pronounced in case of mixed feed strategy compared to methanol feeding. Significant increase in biomass yields and the volumetric interferon productivity [2-fold (methanol/sorbitol) and 0.8-fold (methanol/glycerol)] substantiates the outcome of the thermogram. Calorimetric insight addressed in this study for mixed feed regimes in *P.pastoris* fermentation paves the way for application of metabolic heat rate as a valuable process analytics for monitoring and control of process at technical scale.

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Preparation of pillared layered antimony hydroxide and its flame retardancy in thermoplastic polyurethane

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In this article, a pillared layered antimony hydroxide (LSH) material has been prepared using hydrothermal method. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscope (TEM) results showed that LSH was synthesized successfully. Then the as prepared LSH was added into thermoplastic polyurethane (TPU), and the flame retardancy and smoke suppression of the TPU/LSH composites were examined by cone calorimeter test (CCT), smoke density test (SDT), and thermalgravimetric analysis (TGA). Compared with pure TPU, the peak heat release rate (PHRR) and total heat release (THR) of TPU composites filled with 2 wt% LSH were reduced by 56.1% and 28.3%, respectively. Among all TPU composites, TPU3 (1.5 wt% LSH loading) had the best smoke suppression. Meanwhile, TGA results showed that LSH can remarkably improve the char yield of TPU composites through a Lewis acid catalysis mechanism.

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Cements, building materials

Thermal analysis of Composite Cement with coal

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Keywords: Cement paste, Thermal analysis, Hydration, coal, DSC

The increasing presence of coal as industrial waste is a major threat to the environment. Therefore, we have been obliged were forced (it is high time) to find a scientific solution to stimulate the coal and recycle this huge amount of solid waste as an alternative to ordinary cement. Compared to the conventional cement production, the successful development of this new material can save energy, reduce minimize harmful gas emissions, recycle a huge amount of coal waste, and significantly reduce the cost of cement production, which plays an active crucial role in the construction in the setting of industrial and reconstruction projects. It became necessary to find specifications that fit the purpose required. In the current present experiment, we added multiple doses 10%, 20%, 30%, of the total weight of the material and follow the effect of coal on hydration and the mobility of cement and finding physic-chemical properties and cement by applying the abstract model and the activation energy for each sample. This study was conducted using the differential scanning calorimeter (DSC). The study is both economic in term of cost and it is also environmentally friendly. The results showed that coal is a poisonous substance that contributes leads to the moistening of the cement mix and has contributes to improving the mechanical properties of cement.

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Microstructure and phase characterizations of fly ash cements by alkali activation

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Keywords: Microstructure, phase characterizations, Thermal analysis, Fly ash cements, Alkali activation

Microstructure and phase characterizations of fly ash cement by alkali activation were investigated. High calcium fly ash (FA) at 70%, 80%, 90% and 100% by weight of binders was used in combination with Portland cement (PC) thus producing geopolymer and alkali-activated fly ash cements with some part of Portland cement. Alkali solutions (Na_2SiO_3 and NaOH) were used as activators at alkali liquid/binder of 0.65 and Na_2SiO_3/ NaOH ratio was 0.67 curing at 23°C and 60°C. Scanning electron microscope (SEM) and X-ray diffraction showed sodium alumino silicate hydrate (N-A-S-H) structure and calcium alumino silicate hydrate (N,C)-A-S-H) structures can be found. Thermal analysis results also showed that sodium alumino silicate (N-A–S–H) was detected in all mixes.

Thermogravimetric analysis and phase characterizations of portland fly ash limestone cements

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Keywords: Thermogravimetric analysis, phase characterizations, fly ash, limestone, cements

Fly ash and limestone was used together to replace Portland cement at 50% replacement by weight. Limestone was used at 0%, 5%, 10%,15% and 20% while fly ash was used at 50%, 45%, 40% and 30% respectively. Thermogravimetric analysis (TGA) of the mixes was studied at 7 and 28 days to determine the hydration and pozzolanic reaction occurred during these ages and observe the changes. In addition, compressive strength and physical properties are also given. X-ray diffraction and scanning electron micrograph was also used in combination with TGA for phase characterizations. TGA was used to study the phases such as calcium silicate hydrate, monocarboaluminate, calcium hydroxide and calcium carbonate showing the effect of both fly ash and limestone when these materials were used in combination with Portland cement.

Optimization of cementitious composite for heavyweight concrete preparation using thermal analysis method

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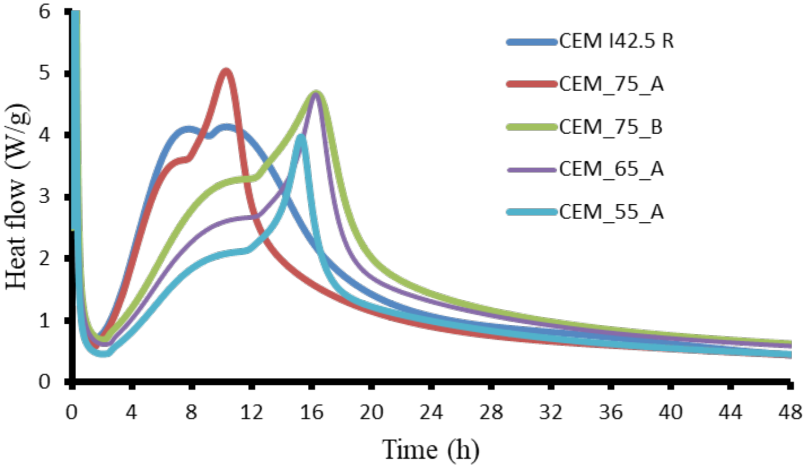
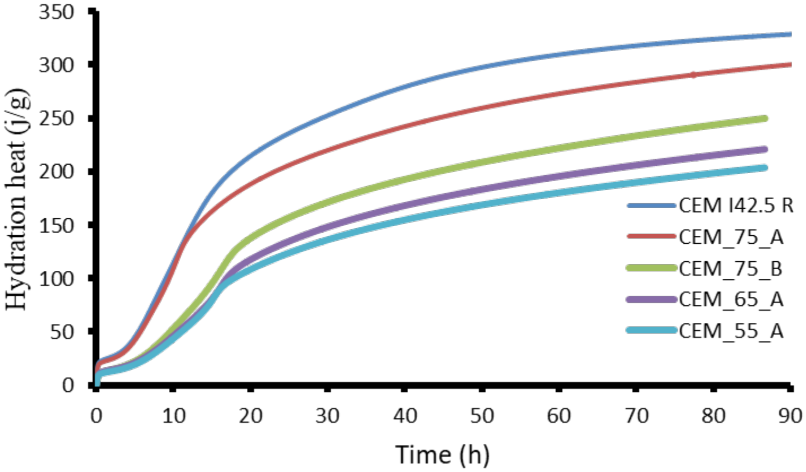
Keywords: concrete mass, hydration heat, thermal shock, SCM, heavy aggregate

Hydration heat of cementitious binders and its rate play key roles in the design of massive concrete structures due to the risk of thermal cracking. Indeed, exothermic hydration reaction of cement generates fast temperature rise in core of concrete structure originating thus temperature difference with concrete surface [1]. As consequence of non-uniform heat distribution and thermal conductivity, the temperature gradient will cause tensile stress. When tensile stress is higher than tensile strength, then thermal crack occurs on the surface of concrete or mortars. Moreover, shrinkage strains at hardening period of cement paste or concrete can be observed [2]. Therefore, the characterization of generated heat of binders is of primary importance in order to assess the early thermal cracking of a concrete structure. The convenient design of heavyweight concrete for massive structure as biological shielding in nuclear plant takes into account, not only the type of aggregates, chemical and mineralogical composition of each component, but the hydration heat and its rate must carefully designated in order to avoid thermal stress, internal and external strain and surface thermal cracking. As cement is the unique source that generates hydration heat, the total amount of generated heat in concrete varies with the type of cements, water-to-cement ratio, initial temperature, admixtures and additives. The partial replacement of cement by supplementary cementitious materials (SCM) leads to the reduction of temperature in hydrating concrete. However, the substitution of cement by SCM lowers strength development at earlier curing period, but contributes to the strength gain at long term age. The present work investigates the hydration heat of different cement composites by means of conduction calorimetry and thermal analysis. Portland cement CEM I 42.5 R was replaced by different composition of supplementary cementitious materials (Blast furnace slag, metakaolin, silica fume/limestone) at 75%, 65%, 60%, 55% and 50% levels. Hydration of seven cement composites and reference one was monitored using TAIM AIR Calorimeter during 90 hours at room temperature. Hydration and its rate depend, not only on replacement level of cement in cement composites, but also on the composition of SCM mixtures.





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Phase transformations in blended g-oil well cements

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Keywords: Dyckerhoff cement, hydrothermal curing, silica fume, ground granulated blast-furnace slag, metakaolin

Following the growing demand to reduce the amount of traditionally obtained energy and on the contrary, replace it by the so-called green energy, among others, also thermal energy, has attracted increasing attention. Cementing in geothermal wells used to be performed with oil well cements that were originally developed for oil and/or gas wells. However, different conditions of high temperatures and higher pressures in liquid or vapour dominated wells impair stability of cementing. Both, the temperature and the pressure influence kinetics of reactions as well as equilibrium state. Even though C-S-H is the first main hydration product regardless of the temperature and the pressure affecting hydration of cement paste, at temperatures above 100 °C, the crystalline α-C2SH and jaffeite (C6S2H3) become more stable phases [1]. Accordingly, depending on the conditions, an equilibrium should be attained between α-C2SH, jaffeite, and portlandite [2]. Transformations of primary hydration products are associated with the decrease of strength and mainly with the increase of porosity [3, 4], which can result in the failure of cementing requiring expensive repairing operations or even new drilling. In order to prevent them, Dyckerhoff cement was substituted by 15 mass% of silica fume (SF), metakaolin (MK), ground granulated blast-furnace slag (BFS) or their combination. Phase changes and their impact on porous structure and compressive strength were investigated up to 28 days of hydrothermal curing at 165 °C and 0.6 MPa. It was proved that the detrimental effect of higher temperature and pressure on the final properties of the designed G-oil well cements depends strongly on their composition. Except composition with SF, jaffeite and α-C2SH were determined in the samples already after short times of autoclaving (6 or 24 h). Neither preferential formation of one nor transformation of one undesired phase to another was demonstrated. α-C2SH was formed in the studied systems, and under the used conditions, a little while before or almost simultaneously with jaffeite formation. However, since the amount of jaffeite did not change significantly with prolongation of autoclaving time, ongoing coarsening of structure resulting in substantial increase of permeability coefficient and decrease of compressive strength depended mainly on the increasing quantity of α-C2SH. The most significant negative changes were demonstrated in referential samples as well as samples containing BFS. On the contrary, partial replacement of Dyckerhoff cement by SF, MK or by their combination seemed to be the most promising for applications in geothermal wells. Especially samples prepared with SF showed character of structure and compressive strength comparable or even better than corresponding samples cured under standard conditions. Acceleration of cement hydration by SF in early times together with its higher reactivity and its much higher fineness resulted in the formation of higher amount of strength possessing phases, as well as more pronounced filler effect, and consequently to more compact structure. Better pore structure of this composition could be explained also by changes in the length of silicate chain, morphology of hydrated products, and larger amount of high density C-S-H, owing to lower C/S ratio and higher temperature.

Acknowledgments

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Desorption of CO_2 adsorbed onto C-S-H gel exposed to natural carbonation

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Calcium silicate gel (C-S-H), the main component of Portland cement was synthesized by the double decomposition method, interchange of two parts of two substances to form two new substances. Samples were kept in the mother solution for 1 week and 4 weeks and after that the solid was filtrated and analyzed by differential thermogravimetric to identify the amount of calcium carbonate formed due to the reaction between the calcium in the solution and atmospheric CO_2. With DTA/TG/MS, mass loss due to water and CO_2 release was observed to take place in intervals unidentified to date, which might be associated with the CO_2 adsorbed on the gel.

Fire resistance performance of concrete panels with PVC stay-in-place formwork

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Keywords: Concrete panels, Fire resistance, Precast concrete, PVC encased system, Stay-in-place formwork.

Stay-in-place (SIP) formwork is an attractive alternative to traditional steel or wood formworks because of its improved constructability and durability. The main aim of the present paper was to study the fire resistance performances of structural and non-structural concrete panels with polyvinyl chloride (PVC) SIP formwork. Three different panels of PVC SIP formwork of dimensions 124.01 in × 110.24 in × 3.15 in were tested and compared to each other. All panels were aged for 28 days, and then exposed to the standard fire curve based on the ISO 834:2014 standard, recording the temperatures in panels' surfaces. The results indicate that concrete strength significantly influenced the structural stability and the fire resistance time of the panels (under load), even in this type of panels when subjected to high temperatures, and that the PVC encasement enhanced the thermal insulation property, one of the fire resistance performance criteria. This alternative for formwork, was considered due to the importance of creating awareness of the need to conserve forest resources and promote their rational use, being this a material friendly to the environment. For the authors, this is the first study on fire resistance for PVC-Concrete constructions.

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Investigations of selected aluminosilicates activity in white calcium aluminate cement hydration

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Keywords: white calcium aluminate cement, hydration, conversion, aluminosilicate addition, thermal analysis

Many different mineral additions e.g. fly ash, granulated blast furnace slag or silica fume are commonly introduced to Portland cement, what brings to economic and environmental benefits and improves the concrete properties. It is important for such materials to be not only a microfiller sealing the cement matrix but also participate actively in reactions via their pozzolanic or/and hydraulic activity [1]. Calcium aluminate cement (CAC) is quite different from the Portland cement in regard of its composition and hydration process chemistry thus the additions interaction on CAC system also differs. Taking into account a transformation of metastable calcium aluminate hydrates formed firstly at low and ambient temperatures to stable products within time or/and with the temperature rising the effect of the mineral additions introduction is even more interesting.

The aim of this work was to determine the activity of two kinds of aluminosilicates in hydrating calcium aluminate cement matrix depending on time of the hydration process at ambient curing temperature. The white calcium aluminate cement containing only calcium aluminate clinker phases was chosen to prove a reactivity of the silica-bearing additions. The hydrates formed were recognized by thermal analysis and X-ray diffraction and the microstructure were observed by SEM/EDX method. The calculation way based on TG results, presented in our previous work [2], was used to estimate the influence of the studied additions on conversion degree of CAC.

On the basis of obtained results it was found, beside typical CAC hydration products, the formation of crystalline stratlingite in presence of both the aluminosilicates instead of hydrogarnet proving the reactivity of the additions in the calcium aluminate cement paste hydrated at the investigated conditions. The confirmed activity of the aluminosilicates was time-dependent and some differences between the interaction of these two additions were found. Moreover the thermal analysis turned to be very useful to find and compare the effect of the minerals on the process [3].

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Application of polymers in building and construction industry

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Keywords: silicates, ceramics, TG, geopolymers, waste

The construction and building industry share a large part of the worldwide market, however the research activity related to these subject is still insufficient. A common theme for research and innovation across this area is to reduce resource consumption and carbon dioxide emissions by creating sustainable system built using eco-friendly technology and construction processes. The construction and building industry share about 40% of global energy-related CO2 emissions [1]. One of the interesting goal is to produce "healthier" binders for concrete production, and this can be realized by using of geopolymers, which are in fact materials similar to natural minerals with repeating units as in organic polymers. This kind of 'mineral polymers' seems to be modern, however their history date back to 25,000 years ago, when terracotta statuette of Venus was created [2]. The synthesis of geopolymers relies mainly on the mixing process of dried pozzolanic material (metakaolin or fly ash) with aqueous solution of different silicates (e.g. sodium or potassium silicate) and addition of a strong base, such as concentrated sodium or potassium hydrate. The resulted material shows behaviour similar to cement, however its production generates about 4-8 times less of CO2 than production of Portland cement. Geopolymers have been also investigated according its potential application in the conservation of tile facades, showing better adhesion to ceramic body compare to the organic polymers [3].

On the other hand, polymeric additives has been widely accepted as a promising for asphalt modification [4,5] or e.g. production of polymer concrete with superior properties, such as higher mechanical strength and chemical resistance [6,7]. Different polymers have been applied in the concrete and cement modification, for example recycled rubber particles that were introduced as aggregates for concrete production affecting on CO2 emissions and energy absorption during deformation of concrete body [8].

In our study we have investigated thermal properties of polymeric materials and organic-inorganic system, that can find potential application in building and construction industry.

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Thermal and structural investigations of cement-based mortars with marble waste fillers

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Keywords: White Portland cement, marble, C-S-H gels, carbo-sulpho- aluminates

Modern trends in the development of building materials are creating materials with low environmental footprint and lower energy costs for their production. These requirements lead to the development of technologies for the production of new building materials where part of the expensive components are replaced by recycled and waste building materials, inert natural minerals and less toxic technogenic products such as cement substitutes to achieve ecological cleanliness and energy efficiency.

In response to current trends in building materials development, the present work explores cement compositions based on white cement and inorganic fillers. White decorative mortars and concretes have restrictions on: white color of the binder and mineral additive, good workability, and a dense structure that does not have significant destructive processes at various atmospheric impacts. In this research are investigated the phase-formation of different cement composites with high content of inert mineral fillers (marble and quartz sand) and different water-cement ratio, obtained after hydration of White Portland cement.

The research is made after 28 and 120 days of water curing. The phase composition (new formed phased as well as formation of C-S-H gels, containing SO_4^{2-}, CO_3^{2-}, OH^-) are defined using X-Ray powder diffraction, Infra-Red Spectroscopy and thermal analysis. The experimental data show that the cement composites with higher water content exhibit variety of new-formed phases, like hydration products of C-S-H type. The use of marble as addition leads to creation of carbo-sulpho- aluminates.

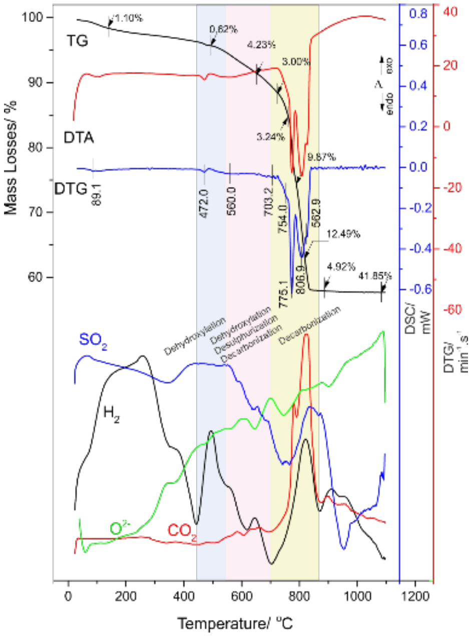

Fig. 1. TG-DTG-DSC of composite of 120 days of curring

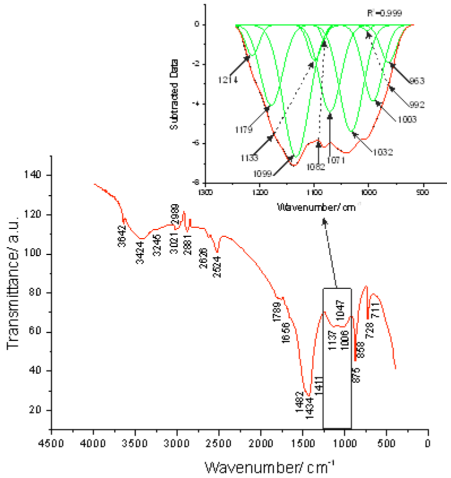

Fig. 2. IR of composite of 120 days of curring

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Ceramics, glasses

Multi-component PZT ceramics obtained by mechanochemical activation and classical technology

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Keywords: multi-component PZT-type ceramics; ferroelectrics; mechanochemical synthesis

In the paper the multi-component PZT-type ceramics admixtures by Mn4+, Sb3+, W6+, Ni2+ were presented. The following chemical composition was designed: Pb(Zr0.49Ti0.51) 0.94Mn0.01Sb0.03W0.015Ni0.01O3. The ceramic powders were synthesized by two methods: (i) the classical technological method using powder calcination and (ii) mechanochemical activation at room temperature. Densification of the powders (sintering) was carried by free sintering method.

In the case of the mechanochemical activation the development of the synthesis has been monitored by XRD and SEM investigations after different milling periods (25 h, 50 h, 75 h). From the obtained powder the PZT-type ceramic samples have been prepared by uniaxial pressing and subsequent sintering.

The ceramic multi-component PZT-type samples were carried out detailed temperature tests, i.e.: DTA, TG, DC electrical conductivity, dielectric properties, as well as XRD, SEM and EDS (Energy Dispersive Spectrometry) research and tests of ferroelectric and electromechanical properties were performed. At the work, a comparison of test results for samples obtained by two methods was made.

X-ray examinations have shown that the obtained material has a perovskite-like structure with a tetragonal phase (close to the morphotropic area). The presented detailed results of the multi-component PZT-type ceramics predispose designed materials in microelectronic applications for example as element of the actuators and piezoelectric transducers. The usage of the mechanical synthesis to obtain the PZT-type materials allows to shortening the time of the technological process, and at the same time not to reduce the electrophysical properties of ceramic samples.

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Thermal analysis techniques applied to study wear mechanisms of black refractories used in the steel continuous casting process

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Keywords: corrosion, submerged nozzle, dilatometry, differential thermal analysis

The continuous advances in the technology of refractory materials promote the development of materials operating at extreme conditions. The effects of different damage mechanisms are critical and it is necessary to provide detailed information about the thermal behaviour of the nozzle-mould flux system, at steel continuous casting process condition. It is possible to describe the attack of the refractories as a complex phenomenon involving not only chemical wear (corrosion), also it is important to consider the combination of physical and mechanical wear. The corrosion affects the internal structure of the nozzles and all the properties. For these reason, it is important a deep understanding and evaluation of the problem in order to prolong the nozzle life in service avoiding the interruption in the continuous casting production and promoting a decrease of the costs on refractories.

Mould fluxes used in the steel continuous casting process provide suitable heat extraction and lubrication [2]. These powders are formed by a complex mix of oxides and carbonaceous materials (coke, graphite, etc.). They also contain fluorite (CaF_2) [3]. Mould flux physical properties (viscosity and surface tension) evolution are strongly dependent on the chemical composition and controls corrosion rate. Both physical properties were determined by experimental tests. For this paper, viscosity is determined by the rotating cylinder method at 1600 ºC and the surface tension is estimated by contact angle measurements using hot stage microscopy (HSM), at similar temperature condition.

The submerged nozzle are constituted with a body of Al_2O_3-C and a insert of ZrO_2-C, in the critic wear zone to protect the material due to the mould flux contact. The structure transformations produced in the refractory material at such conditions also contribute to explain the corrosion mechanisms. In these circumstances the use of thermal analysis techniques (DTA-TG and dilatometry) can provide specific information about phase transformations, mass changes and volumetric variations which occur in the system of study. In this paper, the results are correlated with information obtained through conventional techniques such as optical microscopy (OM) and scanning electron microscopy (SEM) including EDS analysis and EBSD, that are used to characterize different structural aspects on the refractory material and of the interface with the mould flux adhered on the nozzle. The thermodynamic simulation of the corrosion also contribute with relevant information associated to the main goal of this paper. By the thermochemical simulations, the chemical reactions in the system between nozzle and mold flux are justified. All this information is useful to establish the corrosion mechanisms and to predict the dynamic process conditions that cause the damage in the refractory material, in order to improve the nozzle performance.

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Thermal behavior of zirconia/hydroxyapatite composites synthesized by sol-gel method

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Keywords: sol-gel, TG-FTIR analysis, composites, thermal characterization

Composites with chemical formula $xZrO_2(1-x)HAp$, where x=1, 0.9, 0.7, 0.5, 0 indicates the mole fraction of ZrO_2, were synthesized by means of the sol-gel method. Zirconium propoxide solution was used as precursor of zirconia matrix, while, the pure Hap was synthesized using calcium nitrate tetrahydrate and phosphorus pentoxide, as precursors. Finally, the composites were obtained by adding adequate amounts of zirconia sol to the HAp one. The thermal behavior of all the materials, before thermal treatment and after 120° heating, was studied. The TG/DTG curves of all the samples suggest that the thermal treatment at relatively low temperature does not modify the thermal behavior of these composites. The FTIR spectra of the gas mixture evolved during the TG experiments of the fresh samples and of their composites at different temperatures were recorded and the most important results discussed. The results show that in all samples the complete degradation of the organic matter and nitrate ions require heating them up to about 600°C. The XRD spectra of the composite materials treated at 120°C revealed that they are amorphous, while at 600 and 1000°C, their crystallinity decreases with increasing the content of zirconia; the presence of HAp favours the crystallization of the zirconia matrix in the tetragonal phase. SEM microscopy shows that all samples, regardless of the thermal treatment, are homogeneous composites [1]. In conclusion, the results obtained allow identifying the temperatures able to induce specific degradation phenomena that are essential information to develop materials potentially suitable to be used as biomaterials.

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Thermodynamic model and high-temperature raman spectra of BaO-B_2O_3 glassforming melts

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Keywords: thermodynamic model, Raman spectra, borate glass melts

The main aim of the present work is to manifest that the statistical analysis of temperature series of Raman spectra can be used as valuable tool for validation of particular thermodynamic model. The set of 34 baseline subtracted and thermally corrected Raman spectra of BaO-B_2O_3 glassforming melts with the compossition xBaO-(1-x)B_2O_3 ($x = 0.20$; 0.25; 0.30; 0.35; 0.40; 045; 0.50; 0.55; 0.60) measured at temperatures ranging from, 600°C to 1000°C was analyzed. The spectra were recorded with the wavelength step of 2 cm-1 in the wavenumber range of (350–1650) cm-1. The Principal Component Analysis (PCA) indicated six independent components. The Multivariate Curve Analysis (MCR) performed for six independent components resulted in the Raman spectra (so called loadings) and relative abundances (so called scores) of all components. The MCR method reproduced the experimental data with high accuracy – within the experimental spectral noise level. The thermodynamic model of Shakhmatkin and Vedishcheva was evaluated for each glass melt. The molar Gibbs energies of considered system components were taken from the FACT database. Nine following system components (defined as stable crystalline phases of the BaO – B_2O_3 binary phase diagram) were considered: BaO, B_2O_3, 2BaO•5B_2O_3 (Ba2B5), 2BaO•B_2O_3 (Ba2B), 3BaO•B_2O_3 (Ba3B), 4BaO•B_2O_3 (Ba4B), BaO•B_2O_3 (BaB), BaO•2 B_2O_3 (BaB2), BaO•4 B_2O_3 (BaB4). The equilibrium molar amounts of system components were used for evaluation of the molar amounts of basic structural units T_n (trigonal boron with n-bridging oxygen atoms), and Q^4 (tetragonal boron with 4-bridging oxygen atoms). Only three structural units with the mutually uncorrelated equilibrium abundances were found. The Malfaits decomposition was performed for the most abundant units, i.e. T^3 and T^2. Results were compared with the MCR decomposition on two components.

Table I. Components od thermodynamic model and basic structural units.

No	**Name**	**BaO**	**B_2O_3**	***x*BaO**	**Basic struct. units**	***n*(T^3)**	***n*(T^2)**	***n*(T^1)**	***n*(T^0)**	**n(Q4)**
1	'BaO'	1	0	1.000		0	0	0	0	0
2	'B2O3'	0	1	0.000	$2B\O_3$	2	0	0	0	0
3	'Ba2B5'	2	5	0.286	$4[B\O_4]^-$, $6B\O_3$	6	0	0	0	4
4	'Ba2B'	2	1	0.667	$2B\O O_2^{2-}$	0	0	2	0	0
5	'Ba3B'	3	1	0.750	T^0	0	0	0	**2**	0
6	'Ba4B'	4	1	0.800	T^0	0	0	0	**2**	
7	'BaB'	1	1	0.500	$2B\O_2O^-$	0	2	0	0	0
8	'BaB2'	1	2	0.333	$2[B\O_4]^-$, $2B\O_3$	2	0	0	0	2
9	'BaB4'	1	4	0.200	$2[B\O_4]^-$, $6B\O_3$	6	0	0	0	2

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The nitrate and chloride reagents influence on the properties of the resulting nanopowder and on the sintering efficiency of zirconium ceramics from its compacts

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Keywords: nanopowders, sol-gel method, thermal analysis, sintering

Chemical methods for producing nanopowders for the manufacture of ceramics based on partially stabilized zirconium dioxide have great prospects for using in the industry. Among them a special place is occupied by the sol-gel method, since it is characterized by high performance, reproducibility and low cost. In this work, we used the sol-gel method, which is based on the reaction of obtaining a precipitate (gel) of metal hydroxide from a colloidal solution (sol) followed by heat treatment to obtain an oxide. This technology can be implemented using nitrate (technology 1) and chloride (technology 2) zirconium and yttrium salts. Although both technologies involve the production of the same product, it is important to know how the use of each technology will affect the quality of the powder and ceramics. The purpose of this work is to study using methods of thermal analysis in combination with X-ray diffraction methods, laser diffraction characteristics of nanopowders obtained using technology 1 and technology 2, and comparing the characteristics of ceramic briquettes obtained from nanopowders obtained using these technologies. It was established that both technologies allow to obtained nanopowders with an average particle size of 20-30 nm and a specific surface of about 50 m^2/g. Annealing of the initial powder in air proceeds in several stages, depending on the used technology, the common of which is the release of water. With the implementation of technology 1, the release of nitrogen oxides at an annealing temperature of ~ 480 °C was observed. This indicates that part of the zirconium is bound to nitrogen-containing compounds, in order to remove which the powders must be annealed before compacts pressing at a temperature not lower than 500 °C. By dilatometry, it has been established that the effectiveness of shrinking of powder compacts during sintering strongly depends on the type of technology used to obtain the starting powder product. More dense and less porous ceramics may be get on technology 2 using chlorides. The high porosity of ceramics from powders made according to the first technology is due to the release of nitrogen-containing compounds during sintering.

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Thermal proporties of (100-x)(70P_2O_5-30Fe_2O_3)-xNa_2O glasses

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Keywords: iron-phosphate glass, DSC/TG analysis, heating microscopy, Raman spectroscopy

Phosphate glasses are extensively studied due to their potential applications in many fields of science and technology. Calcium phosphate glasses gained interest as biomaterials because of its biocompatibility. Rare earth phosphate glasses have been invested for use in optics, electronics, and optoelectronics. They can also be used in agriculture as fertilizers of slow and controlled dissolution. The most important disadvantage limiting the use of these glasses in some areas is the low chemical durability caused by the existence of easily hydrated P-O-P linkages [1]. However, the addition of iron replaces the P-O-P bonds with more chemically durable P-O-Fe and significantly increase the chemical resistance [2]. The iron phosphate glasses, due to their ability to accommodate relatively large amounts of metal oxides and good chemical durability comparing to borosilicate, may be used as a matrix for immobilization of hazardous waste like toxic or nuclear.

This work presents the results of studies on the thermal properties of glasses with a formal composition of (100-x)(70P_2O_5-30Fe_2O_3)-xNa_2O mol% where x = 0, 10, 20, …, 50. The glasses were prepared from high purity $NH_4H_2PO_4$, Fe_2O_3 and Na_2CO_3. The batch was molten for 2 h at 1200°C in Al_2O_3 crucible in an air atmosphere. The melt was vitrified by casting onto a steel plate and then crushed. The samples were invested with the application of DSC/TG method and observations of shape changes during heating in a heat-stage microscope. The structural changes were investigated using Raman and FTIR spectroscopy.

On the basis of the changes of sample shape in the heating microscope, the characteristic temperatures were determined. The sintering temperature for the glasses was similar and decrease with the increase of sodium content from about 550 to 450 °C. Only the sample with the highest sodium content has a higher sintering temperature than others 660°C due to its partial crystallization. Flow temperatures for the glasses were from the range of 850 – 1130 °C. The lowest flow temperature equal 850°C had the sample with the 40 mol% Na_2O. The DSC curves for all the samples have characteristic for glasses transformation step. The transformation temperature decreases with increasing sodium content. The reverse is the case of specific heat capacity accompanying the glass transformation (ΔC_p). It is increasing from 0.133 to 0.496 $Jg^{-1}K^{-1}$ with increasing sodium content to 40 mol%. The sample with sodium content 50 mol% has lower ΔC_p equal to 0.176 $Jg^{-1}K^{-1}$. Just behind the transformation step, there appears an exothermic effect of crystallization for all the samples. For the low-sodium content glasses, this exothermic effect is small and broad what suggests a complex process of crystallization. The DSC curves for the glasses with the sodium content above 20 mol% are characterized by a strong exothermic effect of crystallization between 500–600 °C. Next, there is evidenced an endothermic effect at about 850 °C. This effect may be related to the melting of crystal phases. The melting temperature indicates that $Na_3Fe_2(PO_4)_3$, $Na_3Fe(PO_4)_2$ or $FePO_4$ phases could recrystallize in these samples. Raman and FTIR spectra show continuous depolymerization of the glass network with the increase of the sodium content in the glass. The glass network is composed mostly of Q^2 and Q^1 phosphate structural units. The number of Q^2 structural units gradually decrease with sodium whereas Q^1 increase. This means that the glass network is built of chains which become shorter with increasing Na_2O content [3]. This leads to a gradual increase in the network flexibility and decrease of the glass transition temperature [4].

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Thermal proporties of iron polyphosphate glasses containing calcium

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Keywords: iron-phosphate glass, DSC/TG analysis, heating microscopy, Raman spectroscopy

Phosphate glasses have large thermal expansions coefficients and low melting temperatures, but their relatively poor chemical durability limits their practical use. The addition of Al, Pb or Fe to glass considerably increases the chemical durability [1]. The iron phosphate glasses due to their ability to accommodate large amounts of metal oxides and high chemical durability may be used as a matrix for vitrification of nuclear wastes. In addition, the glasses have a lower melting temperature than borosilicate due to which they are better suited for immobilization of waste containing large amounts of volatile elements such as Cs. Previous research has shown that the addition of CaO to iron phosphate glasses improved chemical durability [2]. The calcium iron phosphate glasses may be biocompatible and can also be used as biomaterials [3].

The subject of the studies was the effect of CaO addition on thermal properties of 70 P_2O_5-30 Fe_2O_3 mol% glass. The glasses with the addition of CaO in the range from 10 to 40 mol% were prepared from high purity $NH_4H_2PO_4$, $Fe_2O_{3,}$ and $CaCO_3$. The 20 mass % overweight of $NH_4H_2PO_4$ was used to compensate P_2O_5 losses during melting of the batch due to evaporation. The batch was molten for 2 h at 1200°C K in Al_2O_3 crucible in an air atmosphere. The melt was vitrified by casting onto a steel plate and then crushed. The chemical composition of the obtained glass was checked by X-ray fluorescence. Amorphous nature of the investigated materials was confirmed by X-ray diffraction. The synthesized glasses were invested with the application of the DSC method and observations of shape changes during heating in a heating microscope. The structural changes in the glass network were investigated using Raman and FTIR spectroscopy.

The sintering temperatures for samples were similar and they were in the range of 550-600 °C. The flow temperature decrease from 1100°C to 800°C with an increase of the CaO content up to 20 mol%. Further increase of CaO results in a gradual increase of the temperature to 1000°C. The effect may indicate partial crystallization of the high calcium content glasses. From the DSC curves were determined glass transformation (T_g) and crystallization (T_c) temperatures. Additionally, heat capacity accompanying the glass transformation (ΔC_p) was evaluated. The glass transformation temperature decreases from 556 to 526 °C with an increase in the content of CaO to 20 mol % and then slowly increase to 600°C. This may suggest that the glass network flexibility increases up to 20 mol% of CaO. Then the network becomes more rigid what may be a result of the increase of internal strains due to accommodation by the network of large Ca^{2+} cations. The heat capacity change ΔC_p increases with CaO. The effect may be related to an increase of an average bond ionicity due to an increase of ionic Ca-O bonds number. After the glass transformation step, there is observed an exothermic effect which is related to the glass crystallization. In case of the high CaO content glasses, the effect is complex what can indicate the crystallization of the several different crystalline phases. The FTIR and Raman studies showed that the glasses are built of mostly rather short chains composed of Q^2 phosphate units which are terminated by Q^1 units. The number of Q^2 units decreases with CaO. Thus, the phosphate chains become shorter and formation of Q^1-Q^1 dimmers is evidenced.

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Thermodynamic model and raman spectra of BaO-P_2O_5 glasses

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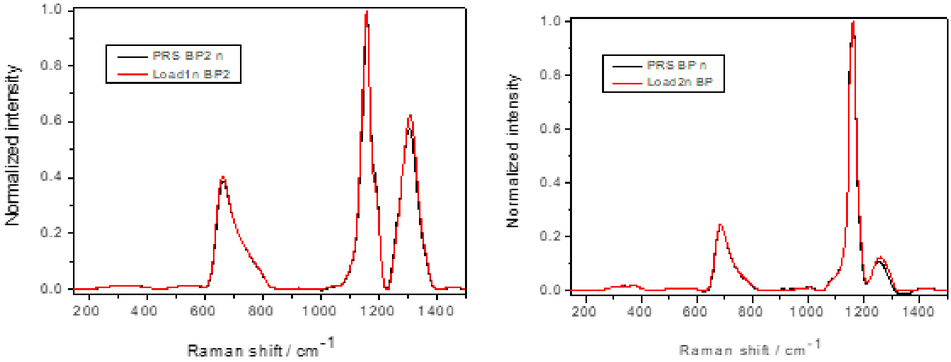
Keywords: Raman spectra, Principal Component Analysis, Multivariate Curve Resolution

The structure of xBaO•(1-x)P_2O_5 ($x = 0.30$, 0.35, 0.40, 0.45, and 0.50) glasses was studied by Raman spectroscopy and thermodynamic model. The thermodynamic model of Shakhmatkin and Vedishcheva was evaluated for each studied glass. Seven following system components (defined as stable crystalline phases of the BaO – P2O5 binary phase diagram) were considered: BaO, P2O5, 4BaO•P2O5 (B4P), 3BaO•P2O5 (B3P), 2BaO•P2O5 (B2P), BaO•P2O5 (BP), BaO•2P2O5 (BP2). Only the equilibrium molar abundances of BP, and BP2 were not negligible in all studied glass compositions. Therefore, in the next step the Multivariate Curve Analysis (MCR) of baseline subtracted and thermally corrected experimental Raman spectra was performed for two components (BP2 and BP). MCR resulted in the Raman spectra (so called loadings) and relative abundances (so called scores) of each considered component. The MCR method reproduced 98.62% of spectral data variance. Then the decomposition of Malfait and Zakaznova-Herzog was used. It can be mathematically formulated as: AP=EC

where $A(N_w/N_s)$ is the matrix of Raman spectra with N_w rows corresponding to N_w wavenumbers and N_s columns corresponding to N_s samples/spectra, $P(N_s/N_s)$ is the square diagonal matrix with the unknown coefficients each multiplying one particular Raman spectrum, $E(N_w/N_c)$ is the matrix of partial Raman spectra (PRS) stored column wise (N_c equals to the number of independent components), and $C(N_c/ N_s)$ is the matrix with abundances of N_c individual components in N_s samples (equilibrium molar amount of BP2 and BP in our case).

MCR results (loadings and scores) has to be compared with Malfait's decomposition (partial Raman spectra) and equilibrium molar amounts of system components (BP2 and BP).



Normalized PRS of BP2 versus normalized Loading 1 and PRS BP versus normalized Loading 2

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Thermal behaviour of some glass and stone wools

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Keywords: glass wool, stone wool, thermal stability, insulating materials, SEM, elemental composition

Some thermal properties of glass and stone wool of three different manufacturers were studied using the two most common methods of thermal analysis, thermogravimetry (TG) and differential scanning calorimetry (DSC). It is known that stone wool can withstand more than 800 °C without melting whereas glass wool begins to soften already above 500°C, which is due to the glass transition of amorphous SiO2. An organic binder, which coats fibers of both types of wools, enabling them to settle in the production process and compress them in the layers, starts to decompose already at lower temperatures. TG results show that in the case of stone wools, the thermal decomposition of the organic binder takes place in the temperature range between 200 and 550 °C (mass loss is about 4%) and for glass wools this temperature range in between 200 and 600 °C (mass loss is higher, between 7 and 11%). DSC curves of glass wool samples exhibit a broad endothermic change in a temperature range between 400 and 720 °C with a peak at about 670 °C. Enthalpy change probably occurs due to the breakdown of the organic binder and consequently heat capacity changes; as well due to the glass transition. DSC curves of stone wool samples also show endothermic changes in the range of 450 to 800 °C. From the appearance of intermediates, treated to different temperatures, it is obvious that the stone wool fibers still retain their shape even when heated to 1100 °C while glass wool fibers completely lose their shape already around 800 °C.

The size, shape and surface of mineral fibers were monitored by field emission scanning electron microscopy (FE-SEM), while elemental composition of the samples was determined using energy dispersive X-ray spectrometry (EDS). The diameter of both types of fibers is between 5 and 10 μm; the stone wool fibers are more straight. Line analysis of elements, perpendicular to glass fiber, indicates that the main component of the glass fibers is silicon, followed by oxygen, sodium, calcium and magnesium; while the major constituent of the stone wool fibers is oxygen, followed by silicon, magnesium, calcium and sodium. The elements are evenly distributed in the fibers. Fluorine was detected on the surface of glass fibers, thermally treated at 200 and 400 °C, while its signal disappeared after thermal treatment at 600 °C. It is therefore assumed that this element is present in the organic binder. In the case of the stone wool samples, a very small proportion of fluorine was present throughout the whole cross-section of the stone fiber.

Magnesium doped calcium silicate nanobioceramics for hard tissue regeneration

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Keywords: calcium silicates, ceramics, nanobiomaterials, tissue engineering

Nanotechnology has been tremendously expanding through the last years concerning bone regeneration. The biological activity of calcium silicate ceramics has gained the most research interest due to their great potential to affect the *in-vitro* osteogenesis and *in-vivo* bone tissue regeneration [1]. Incorporation of Mg in the Ca-Si system could be suggested for the synthesis of various structures, such as scaffolds or nanoparticles, for hard tissue regeneration [2], as they present high residual glassy phase, high hardness values, hydroxyapatite-forming ability and biodegradable properties. Also, when they are used in combination with a polymeric matrix, they exert an enhancing effect on the mechanical properties. Nano-bioceramics are advantageous compared to their micro-scale counterparts, because of their increased surface area, enhancing mechanical properties and apatite-forming ability due to the increased nucleation sites [3]. The purpose of the present work was to study the bioactivity behaviour in relation to the thermal behavior of the tertiary system SiO_2-CaO-MgO (60, 35 and 5%mol respectively). The synthesis was held via sol-gel method according to literature [4]. The glass was heat treated at 835°C, 903°C, and 1100°C after TGA analysis and the optimum thermal conditions for bioactivity were evaluated. Apatite forming ability evaluation was conducted by the immersion of the samples in c-SBF for 1, 3, 5 and 10 days under renewal conditions [5]. TGA/DSC, FTIR, XRD and SEM/EDS were used for the characterization of the samples. The results showed that with the temperature increase, the crystallinity of the ceramics was increased; instead the percentage of the amorphous phase was reduced. Bioactivity tests showed that apatite formation was already distinct from the first day in all three cases but the most bioactive glass was the heat treated at 835 °C, which had the highest amount of the amorphous phase. This was evidenced by the double peak at 610-600 and 560-550cm^{-1} after 3 days of immersion and the sharp peak at around 1090cm^{-1} In conclusion, the more amorphous the bioceramic is, the highest bioactivity it presents. Thermogravimetric analysis (heating rate 10°C/min, air atmosphere) indicates a total mass loss of 45%, which was attributed to desorption of physically adsorbed water and evaporation of $HNO_{3,}$ and at higher temperatures to the decomposition of the nitrate content of the sol-gel reagents and the removal of the chemisorbed water. Heat flow curve indicates the presence of a main crystallization peak at 950°C and a secondary at 1288°C.

Acknowledgments
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Crystallization kinetics of gehlenite glass microspheres

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Keywords: flame synthesis, gehlenite glass microspheres, crystallization kinetics

The gehlenite ($Ca_2Al_2SiO_7$) glass was prepared by flame synthesis in the form of glass microspheres [1]. The powder precursor for flame synthesis was synthesised by standard solid state-state reaction method using SiO_2, Al_2O_3 and $CaCO_3$ as starting materials. The prepared glass microspheres were characterized from the point of view of surface morphology, phase composition and thermal properties by optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC), respectively. The prepared glass microspheres were XRD amorphous. The amorphous character of glass microspheres was further verified by SEM microscopy (Fig. 1.). The high temperature X-ray powder diffraction measurements (HT XRD) were carried out in the temperature interval 600-1100°C to identify the phase evolution during glass crystallization. In studied temperature range only gehlenite phase was identified (Fig. 2.). Non-isothermal DSC analysis of prepared glass microspheres was carried out from room temperature up to1200°C at five different heating rates: 2, 4, 6, 8 and 10 °C/min. From the DSC analysis the glass transition temperature (T_g), onset of crystallization (T_x), temperature of the inflection point of the crystallization peak (T_f) and the crystallization peak temperature (T_p) were determined. In order to study the crystallisation kinetics, the DSC curves were transformed into dependence of fractional extent of crystallization, α on temperature. The Johnson-Mehl-Avrami-Kolmogorov (JMAK) [2] model was found to be suitable for description of crystallization kinetics. Frequency factor A , apparent activation energy Eapp and the Avrami coefficient m was determined (Tab. 1.) using RSS, R^2_{adj}, and AIC criteria.

Tab.1. The calculated kinetics parameters

Sample name	**A [min^{-1}]**	**E_{app} [$J.K^{-1}.mol^{-1}$]**	**m**
Gehlenite	$5.56.10^{29}$	$7.22.10^{5}$	2.0

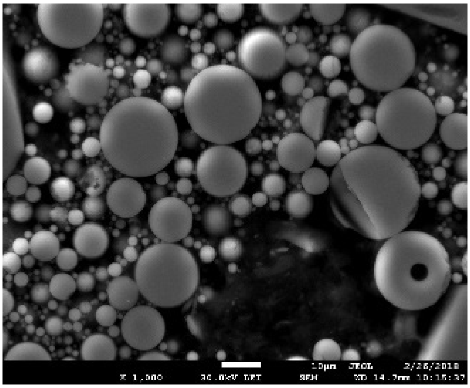

Fig.1. SEM micrographs of polished surface of the microspheres
gehlenite glass microspheres

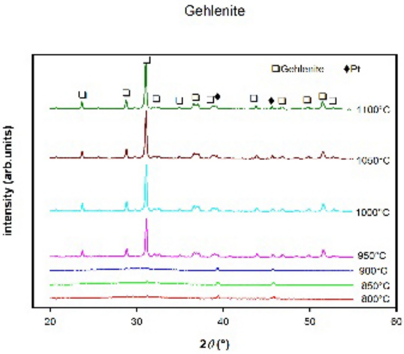

Fig. 2. HT XRD records of the gehlenite glass recorded at various temperatures

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Electrophysical properties of the multiferroic PFN-ferrite composites obtained by spark plasma sintering and classical technology

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Keywords: multiferroics, ferroelectric–ferromagnetic composites, PFN ceramics, ferrites

In the paper the multiferroic (ferroelectric-ferromagnetic) composites (PFN-ferrite) based on ferroelectromagnetic PbFe1/2Nb1/2O3 powder and ferrite powder (zinc-nickel ferrite) were obtained in the presented study. The ceramic PFN-ferrite composites consisted of 90% powder PFN material and 10% powder ferrite powder. The ceramic powders were synthesized by the classical technological method using powder calcination, while densification of the composite powders (sintering) was carried by two different methods: (i) by Free Sintering method (FS), and (ii) by Spark Plasma Sintering (SPS).

The composite PFN-ferrite samples were thermally tested, including: DC electrical conductivity and dielectric properties. At room temperature the following tests were carried out, too: XRD, SEM and EDS (Energy Dispersive Spectrometry) and ferroelectric properties (hysteresis loop) of the composite samples. At the work, a comparison of measurement results for PFN-ferrite composite samples obtained by two methods was made.

X-ray examinations of multiferroic ceramic composites confirmed the occurrence of the strong diffraction peaks derived from ferroelectric (PFN) matrix of composite as well as weak peaks derived from the ferrite component. At the same time, the studies showed the absence of other undesired phases

The result of measurements presented in the work revealed that the ceramic composite obtained two by different technological sintering method (Free Sintering method and Spark Plasma Sintering technique) can be promising materials for functional applications for example in sensors for magnetic and electric field.

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Dilatometric analysis of sintering lithium-zinc ferrite ceramics

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Keywords: lithium ferrite, dilatometric analysis, mechanical activation, sintering.

Ferrites are key elements in most modern radio engineering, electronic and computing devices, including lithium ferrites, which are widely used in microwave technology, and as cathodes of lithium batteries. Substituted lithium-zinc (LiZn) ferrites with the chemical composition of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ are characterized by high values of saturation magnetization and Curie temperature and, thereby, provide active interaction with electromagnetic waves at the low frequency band of the microwave range. The ceramic technology is conventional way to produce ferrites, which involves both the synthesis of ferrites with the formation of single-phase ferrite compositions (via solid-state reaction with oxides/carbonate) and further sintering at high temperatures to produce high-density ferrite ceramics. Because of complex composition of reaction mixtures, repeated alternation of grinding and thermal treatment operations is often performed for completeness of solid-phase reactions, thereby significantly increasing the time of synthesis. A mechanical activation procedure, that is ball milling the reagent mixture in a high energy ball mill, is widely used to increase the reactivity of reagents and reduce the temperature and time of synthesis. The aim of this work was to study of a one-stage production of high-density Li-Zn ferrite ceramics by heating pre-mechanically activated Fe_2O_3-Li_2CO_3-ZnO reagent mixture in order to exclude the stage of preliminary synthesis procedure. The ball milling was performed in a AGO-2S (Novic, Russia) high energy planetary ball mill with steel grinding balls using centrifugal accelerations of 1000 m/s^2. The milling time was 60 min. The samples from milled mixture were compacted by cold pressing in the form of pellets in a PGr-10 hydraulic press at 200 MPa for 3 min. The sintering of powder compacts was conducted in a DIL 402 C (Netzsch-Gerätebau GmbH, Germany) dilatometer using different heating rates of 2, 5, 10 °C/min and an isothermal aging at 1050 °C for 1 h . XRD analysis of the powder mixtures was performed using POWDER CELL 2.5 software. An ARL X'TRA powder diffractometer (Switzerland) was used for the analysis. Phase identification was performed using the PDF-4 powder database of the International Center for Diffraction Data (ICDD). The model-fitting kinetic analyses of ferrite densification were performed by using full DIL data and Netzsch Thermokinetics software. The electro-magnetic parameters for ferrite ceramics were estimated. It was established that preliminary ball milling the initial reagent mixture in the planetary mill allows not only to accelerate the solid-phase reactions, but also to combine the both technological stages of synthesis and sintering in one stage of thermal treatment. Li-Zn ferrite ceramics obtained is characterized by high density and low porosity as well as high values of the specific magnetization and the Curie temperature.

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Crystallization of $Ln_2Ti_2O_7$ (ln = Gd, Lu) using co-precipitation method: carbon in pyrochlores

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Keywords: pyrochlore, titanate, co-precipitation, crystallization, carbon

$Ln_2M_2O_7$ (Ln = La-Lu; M = Ti, Zr, Hf) pyrochlores belong to the large class of compounds, which show different structural, chemical, physical properties. $Ln_2Ti_2O_7$ with pyrochlore structure are promising ceramic materials for production of solid electrolytes for high-temperature solid oxide fuel cells (SOFCs).

Rare-earth titanates are typically prepared via coprecipitation or sol–gel processing, followed by high-temperature heat treatment [1–3]. In a number of cases, the final product had deviations from stoichiometry according to XRD data, and contained up to 3 wt % carbon [3]. The likely reason for the deviations from stoichiometry and the presence of carbon in materials prepared via coprecipitation is that, during the coprecipitation process, the $Ln(OH)_3$ (Ln = Gd-Lu) hydroxides absorb CO_2 from air and partially convert into X-ray amorphous $LnOHCO_3$• nH_2O basic carbonates [4].

The purpose of this work was to find out the cause of the hindered crystallization (ongoing decrease in the lattice parameter) of the $Ln_2Ti_2O_7$ (Ln = Gd, Lu) pyrochlores in a wide temperature range, from 700 to 1600°C. We studied as-precipitated precursors (1) and samples heat-treated in air for a long time (2–5) under the following conditions: 550°C for 22.5 days (2), 700°C for 9 days (3), 1200°C for 54 h (4), and 1500–1600°C for 10 h (5). The powders thus prepared were characterized by XRD and DTA/TG in combination with mass spectrometric analysis of the gas released during heating at 10°C/min to 1200°C in oxygen or helium containing 0.1% oxygen. According to XRD data, the as-prepared precursor (1) consisted of an amorphous phase and a small amount (<5%) of $LnTiO_3$ and/or Ln_2TiO_5, sample 2 consisted of only an amorphous phase, sample 3 had broadened reflections from the pyrochlore phase and contained a residual amorphous phase, and samples 4 and 5 consisted of a crystalline $Ln_2Ti_2O_7$ (Ln = Gd, Lu) pyrochlore phase. Heating the samples in a DSC cell was accompanied by a multistep gas release, usually in parallel with a weight loss and thermal events. The most interesting data were obtained for samples 4 and 5, synthesized at 1200 and 1600°C. Even though no XRD evidence for the presence of carbon in the pyrochlore phases was obtained, heating these samples was accompanied by CO_2 release, a weight loss, and exothermic peaks between 350 and 600°C. Additional experiments in He containing oxygen impurities showed that CO_2 formation was due to the oxidation of carbon with oxygen from the gas phase. At higher temperatures, we observed an increase in the amount of released CO_2, with broad maxima in the range 800–1000°C. Despite the carbon "burnout," the sample weight was found to increase at these temperatures, attesting to the oxidation of the reduced precursors.

In the case of the precursors (1) and amorphous sample (2), we observed gas release between 100–400°C (H_2O+CO_2, endotherm, and $\Delta M/M=20\%$ for sample 1; CO_2, and $\Delta M/M=0.7\%$ for sample 2) and CO_2 release in the ranges 400–650 and 750–800°C. In the last case, CO_2 formation was accompanied by an exothermic peak and a noticeable weight loss, pointing to the pyrochlore crystallization onset. Above 800°C, we observed a gradual increase in the signal from CO_2 over the sample. The presence of basic carbonates can limit the gradual decrease in the lattice parameter of the pyrochlores during phase formation in the range 700–1600°C. Thus, after thermal annealing at 1500–1600°C, the synthesized pyrochlore phases contained more than 0.5% amorphous and/or lattice carbon, which was difficult to remove from the sample. Carbon "burnout" from crystalline pyrochlore phase lead to CO_2 release between 600 and 800°C and can effect on the anomalous behavior of the permittivity of the rare-earth titanates in this temperature range [5].

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Phase formation of Ln2Hf2O7 (Ln = Nd, Dy) using mechanical activation method. carbon in hafnates.

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Keywords: pyrochlore, fluorite, hafnate, mechanical activation, ball-milling, carbon

The lanthanide hafnates $Ln_2Hf_2O_7$ (Ln = Nd, Dy) belong to the large class of compounds, which show different structural, chemical, physical properties. Rare-earth hafnates are typically prepared via coprecipitation, sol–gel processing or mechanical activation (m/a) of oxides, followed by high-temperature heat treatment at 1600-1650°C [1, 2]. In some cases, on the XRD pictures of hafnates synthesized at 1600–1650 ° C, it is noted the presence of the line 26.6 ° in 2θ (CuKα), which refers to graphite [2]. The likely reason for the presence of carbon in materials prepared via m/a is that, during m/a process, the Ln_2O_3 (Ln = Nd, Dy) absorb CO_2 and H_2O from air and partially convert into X-ray amorphous $LnOHCO_3 \bullet nH_2O$ basic carbonates [3].

The purpose of this work was to determinate the phase formation features of $Nd_2Hf_2O_7$ pyrochlore and $Dy_2Hf_2O_7$ ($DyHfO_{4-\delta}$) fluorite in a wide temperature range, from 550 to 1600°C. We studied precursors (1) obtained using mechanical activation and samples heat-treated in air for a long time (2–5) under the following conditions: (2) 550°C, 22.5 days; (3) 1200°C, 54 hrs; (4) 1600°C up to 10 hrs. The powders thus prepared were characterized by XRD and DTA/TG in combination with mass spectrometric analysis of the gas released during heating at 10°C/min to 1200°C in oxygen or helium containing 0.1% oxygen. According to XRD data, the as-prepared precursor (1) consisted of a mixture of start oxides, sample (2) consisted of start oxides with wider diffraction lines, sample (3) consisted of well-crystallized $Nd_2Hf_2O_7$ pyrochlore with HfO_2 admixture and phase-pure $DyHfO_{4-\delta}$ fluorite, and samples (4) consisted of a phase-pure $Nd_2Hf_2O_7$ pyrochlore and $DyHfO_{4-\delta}$ fluorite phase, respectively. Heating the samples in a DSC cell was accompanied by a multistep gas release, usually in parallel with a weight loss and thermal events. The most interesting data were obtained for samples (3) and (4). Even though no XRD evidence for the presence of carbon in the hafnates was obtained, heating these samples was accompanied by CO_2 release, a weight loss, and exothermic peaks between 300 and 450°C. It is shown that the CO_2 formation is due to the reaction of carbon with O_2 (g). At higher temperatures, we observed an increase in the amount of released CO_2, with broad maxima in the range 600–1000°C. For samples (1) and (2), the CO_2 release also accompanies the start of the synthesis of final products. It should be noted that main synthesis from mechanically activated oxides occurs in the region of 800–900°C for $Nd_2Hf_2O_7$ and 1000–1100°C for $DyHfO_{4-\delta}$, respectively, and is accompanied by weight loss, which is more significant in the first case than in the second. In general, all effects associated with the CO_2 release are less pronounced for the synthesized $DyHfO_{4-\delta}$ fluorite than for the $Nd_2Hf_2O_7$ pyrochlore.

Thus, after 1600°C thermal annealing, the synthesized pyrochlore and fluorite phases contained more than 0.2–0.4% amorphous and/or lattice carbon, which was difficult to remove from the samples. Carbon "burnout" from crystalline pyrochlore and fluorite phases lead to CO_2 release between 600 and 900°C and can effect on the anomalous behavior of the permittivity of the rare-earth haftanes in this temperature range.

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Temperature dependence of electrical resistivity and absolute thermoelectric power of $Co_{71}Fe_4Si_{10}B_{15}$ amorphous magnetic alloy

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Electronic transport properties are very sensitive to the structural changes and can be used to determine the phase transitions which results in a obviously decrease in the values of resistivity (ρ) and Absolute Thermoelectric Power (ATP), as function of temperature or the alloy considered passes from the amorphous state to the crystalline state under the effect of heat treatment [1]. The electrical resistivity (ρ) and absolute thermoelectric power (ATP) or Seebeck coefficient (S) of the amorphous $Co_{71}Fe_4Si_{10}B_{15}$ alloy have been measured as function of temperature from the room temperature to 700°C. The aim of this work is to analyze the structural phase transformation and the crystallization process of this sample. A new method was used to measure accurately, simultaneously or separately resistivity and thermopower, which called the ”six-probe technique”, instead the old one (four- probe technique), In order to ensure good resistivity measurement accuracy at high temperature, we calibrated the sample around the ambient temperature. In fact, the calibration makes it possible, at ambient temperature, to check or correct the geometric constant and to adjust it exactly in the device at high temperature by means of a polynomial or linear equation determined from the measurements of the calibration.

The curves show that the crystallization begins at 495°C and ends at 540°C, at this temperature the sample becomes completely crystallized

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Thermal Analysis and Biological Properties of hybrids based silica synthesized via Sol-Gel

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Keywords: Sol-Gel, FTIR, TG, SEM

In this work, organic-inorganic hybrids, consisting of an inorganic silica matrix (SiO_2) with a high amount of polyethylene glycol (PEG 60 and $70_{wt\%}$), were synthesized via sol-gel. The chemical structure of the obtained SiO_2/PEG 60 and $70_{wt\%}$ was investigated by Fourier transform infrared (FTIR) spectroscopy. In the spectra of both samples, all the typical bands of the silica sol-gel materials are present but with reduced intensity. Moreover, some polymer bands whose intensity increases with the PEG amount are observed. The thermal behavior of the obtained gels was investigated by Simultaneous thermogravimetry/differential thermal analysis (TG/DTA) to establish the best temperatures for their heat treatment. The cross-section surface morphology of the materials was observed using a scanning electron microscopy (SEM). The micrographs showed that no significant differences were present between the samples and that the materials are homogeneous. No phase separation was visible even at high magnifications. Therefore, the synthesized materials are nanocomposite hybrids. *In vitro* bioactivity tests were carried out by soaking the samples powders for 21 days in Simulated Body Fluid (SBF). SEM/EDS microscopy allowed to detect the deposition of spherical formations with the typical apatite morphology on the materials surface. Cytotoxicity assays were performed using a WST-8 assay, a colorimetric test. The NIH-3T3 murine fibroblast cell line (ATCC, USA) were grown in DMEM medium (Gibco, CA, USA) and treated with the extracts of the materials. The best results were obtained with $70_{wt\%}$ of PEG.

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Synthesis of glasses for obtaining fusible protective coatings for steel products

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Keywords: glass-enamel coating, corrosion resistance, steel pipelines, protective coating

Glass-enamel coatings based on an alumino-boro-silicate glass in the system K2O – Na2O –Li2O – CaO – CuO – MnO – Al2O3 – B2O3 – CoO – NiO – TiO2 – SiO2 – F- are the most reliable and versatile among corrosion-protective coatings for steel products [1-2]. These anti-corrosion coatings not only improve chemical resistance but also contribute to the improvement of other technical and operational properties of steel products, including pipelines. The development of such protective glass-enamel coatings in practice is a rather complicated problem. In this case, it is economically feasible to use only single-layer enamels, the composition, and properties of which provide high-performance properties of products in a single thermal treatment. At the same time, the coating should be formed without defects at relatively low temperatures in order to prevent steel from warping and softening because of polymorphic transformations in the structure of iron at high temperatures [3-4]. On the other hand, this coating should have a high corrosion resistance to various aggressive and abrasive media. Moreover, coating defects exposing metal are not allowed since corrosion destruction begins on unprotected areas due to electrochemical processes. Therefore, during the study, the glass matrix was synthesized in the temperature range of 1250–1300 °C for 60 minutes. Single-layer glass-enamel coatings for the inner surface of steel pipelines were obtained by high-temperature treatment (820–850 °C) for 3-5 minutes. The influence of the technological and high-temperature treatment parameters of glass-enamel coatings on steel (temperature, duration, coating thickness, etc.) on their structure and properties was investigated. The physical-chemical and technological properties of glass-enamel coatings were studied, such as TCLE 110·10-7 °C-1, flowability 43 mm, impact strength 2.2 J, density 2.4 g/cm3, tensile strength 110 MPa and adhesion strength 4 points. The corrosion resistance of the resulting coatings to water, acid and alkali was also studied. The mass loss of glass, which characterizes acid resistance, after exposure to boiling 20% aqueous hydrochloric acid for 2 hours does not exceed 0.65 %. The mass loss of glass, which characterizes alkali resistance after exposure to 4% aqueous sodium hydroxide solution for 2 hours, does not exceed 1.6%. The water resistance of glass corresponds to the hydrolytic class “2/98”. Thus, a single-layer glass-enamel coating of an optimal enamel composition to protect steel products, including pipelines was synthesized. The modes of its application and thermal treatment were studied and the optimal parameters were described.

Acknowledgments

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Cultural heritage

Investigation of clay minerals in archaeological ceramics by thermal analyses (STA, DIL) and IR

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Keywords: ceramics, rehydroxylation, clay minerals, STA, IR, XRD, archaeology

Identification of sources of raw materials is the principal issue of the most of archaeological ceramic findings studies. Correct interpretation of the performed analyses is based on the knowledge of processes which proceed during temperature treatment of assumed raw materials. This work is focused on the identification of clay minerals, especially kaolinite a montmorillonite, in ceramic bodies and also in original raw materials. Clay minerals identified in archaeological ceramic samples could be from a primary source or products of ageing of ceramic bodies, i.e. rehydroxylation of meta-clays. Accelerated rehydroxylation process can be simulated in laboratory conditions in an autoclave [1]. Fine grained sections of ceramic bodies containing meta-clays of selected archaeological finds were treated in hydrothermal conditions (HT). Qualitative and quantitative changes of presented clay minerals were studied by several method such as XRD, STA and IR.

The rehydroxylation process was studied in following archaeological objects: a moon-shaped idol from the Bronze Age – it was proved that kaolinite in the border parts originated from raw material and that its presence in the central part was caused by the rehydroxylation process [2]; a mosaic Gothic pavement – it was proved that white highly destructed parts of tiles were made of kaolin [3]; a relief Romanesque pavement – hydrothermal treatment and subsequently performed analyses proved the presence of montmorillonite [4], a Renaissance ceramic distillation apparatus – hydrothermal treatment and subsequently performed analyses proved the presence of kaolinite.

The presented work shows that identification of clay minerals by the suitable hydrothermal treatment and subsequently performed analyses can considerably help in determination of source materials and firing temperatures of the studied archaeological findings.

Acknowledgments

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TG-DTA and FT-IR analyses of various samples of mortars from Deva region

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Keywords: Thermal analysis, infrared spectroscopy, historical

Thermal analysis and infrared spectroscopy are used in the study of various mortar samples clearly framed in different historical periods in the Deva area (Romania). The results obtained will clarify the character of a certain samples, several medieval mortar samples, another from possible Dacian mortar, while another was not even certain to be mortar. The results may contribute in the successful dating of the samples. The area under investigation is of great importance for Romanian culture, so restorers have to find and produce mortars similar to those used in the building of our monuments. The thermoanalytic curves obtained in the case of possibly Dacian and medieval mortars are presented in Figures 1 and 2.

FTIR Spectra were collected in the 4000-650 cm-1 spectral range, using a PerkinElmer SPECTRUM 100 (UATR-FTIR). The thermal behaviour for all of the samples was recorded in the air atmosphere with a flow rate of 100 ml·min-1, using a heating rate of 20 °C·min-1 until 1300 °C on a TG/DTA Diamond thermobalance produced by Perkin Elmer in alumina crucible.

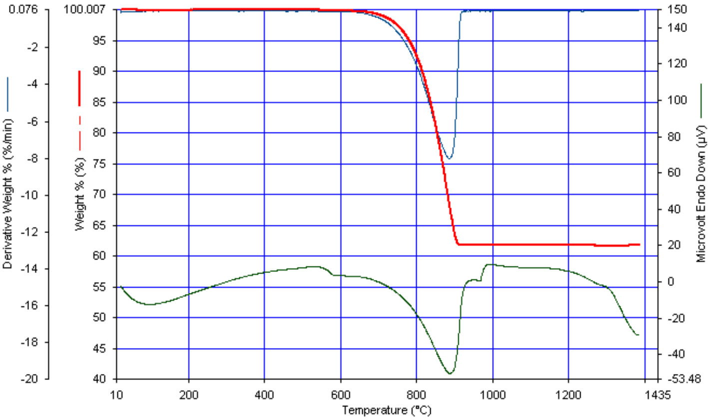

Fig. 1. The thermoanalytical curves at heating rate of 20 °C·min^{-1} to 1300 °C in air atmosphereof dacian mortars

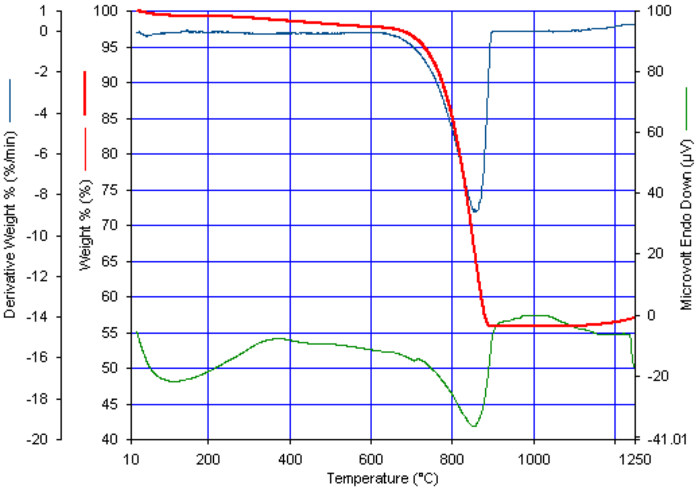

Fig. 2. The thermoanalytical curves at heating rate of 20 °C·min-1 to 1300 °C in air atmosphereof medieval mortars

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Energetic materials

Square ribs size influence on dissipated heat removing from the rear side of PV panels through a back-mounted channel

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Keywords: Natural Convection, Numerical Simulation, Vertical Back Mounted-Channel, Dissipated Heat Removing, Ribs Size, Asymmetric Heating.

In this paper, the heat removing from the rear of PV panels through a back-mounted channel or when the PV panels are integrated in building as a double skin facade was numerically studied. In fact, the effect of size of two adiabatic square ribs on dissipated heat removal from the back-side of PV panels and flow dynamic within the back-mounted channel is investigated. The two square ribs are symmetrically installed above the heated zone on each wall of the back-mounted channel. This later is represented by an asymmetrically heated channel immerged in water tank (its environment). The use of water is to neglect radiation effect. In the computational procedure, the bi-dimensional continuity, momentum and energy equations in the unsteady state were resolved using finite volume method. Three ribs sizes are studied, namely Rd = 1/18, 3/18 and 6/18. The numerical study was undertaken under realistic environmental and geometric conditions, i.e. the considered heat flux density (q" = 510 W/m2) corresponds to the average annual solar heat flux in France, and the value of the channel aspect ratios Rf, it is within the range of those found for horizontally divided double-skin facades of high-rise buildings. The considered modified Rayleigh number based on the two later parameters is equal to Ra* = 4.5×106. The current numerical results were compared with those experimental and a very good agreement was found. Also, it is noticed that the ribs size variation has a strong effect on heat transfer and fluid flow within the back-mounted channel. Furthermore, an optimal ribs size is detected.

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Mixing of Solid Refused Fuel Particles in a Bubbling Fluidized Bed: Experimental and Numerical Studies

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Keywords: mixing, SRF, fluidized bed, fluidization velocity, bed-particles-size

In this work, experimental and theoretical studies have been carried out to investigate the mixing of Solid-Refused Fuel (SRF) particles in a bubbling fluidized bed. The investigations include the effect of fluidization velocity ratio and the bed-particles-size. The experiments were performed on a pilot-scale cold-flow fluidized bed. The bed material (sand) and the SRF particles have average particles-diameters of (d_{pm} = 654,810 and 1110µm < sand >, and d_{pm} = 3520µm < SRF >). The SRF axial concentration was measured using the Bed-Frozen Method at three axial locations within the bed, namely the bottom, the middle, and the top. The bed composition was initialized in three segregate layers containing binary mixture (flotsam and jetsam). The flotsam material (middle layer) contained SRF of different shapes and sizes and the mean diameter of flotsam is equal to (3520 µm), while three sand (jetsam) samples of different mean sizes (654, 810, and 1110 µm) were used in the experimental investigations. The experimental measurements were carried out on an adiabatic-basis (cold-flow at room temperature) as follows:

1. Measuring minimum fluidization velocity of the jetsam mixture (from the pressure drop curve of the jetsam particles).
2. Each of the two particulate materials flotsam and jetsam were initially placed in separate layers in a sequence jetsam-flotsam-jetsam from the bottom with a total static bed height of 10 cm and flotsam weight ratio of (30 gm SRF/3500 gm sand).
3. The blower was switched on and the speed controller was adjusted to give the desired flow rate and fluidization air velocity.
4. The fluidization operation was performed until reaching a steady-state experimental condition. In the present study, it was taken as 20 minute which was found sufficient [1, 2] to ensure steady state.
5. After the fluidization duration, the gas flow was suddenly cut-off and the external separation plates were introduced at each of the two separation slots.
6. Each separated section was sieved individually to collect the separated flotsam and jetsam particles for weighting them.
7. The previous procedure was repeated at different fluidization velocities times of the minimum fluidization velocities.

The theoretical CFD model is based on the finite volume Eulerian-Eulerian approach. The CFD model showed overall acceptable agreement with the experimental data of this heterogeneous system when assuming the SRF particles as disks of sphericity ratio of 0.23. The results showed that in the bed body (middle) regime, the relative mass fraction of SRF was exhibiting a rising trend at low fluidization velocities ($u/u_{mf} = 1.2 \sim 1.6$) and over this range, the SRF concentration stabilizes around a saturation value of ~ 33.5%. Increasing the inert bed particles size was found increasing the SRF concentration in the middle and the top layers of the bed.

Acknowledgments

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Determination of the Thermal Kinetics parameters of Gun Propellant

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Keywords: kinetic parameters, gun propellants, thermal stability, auto-ignition.

The thermal stability of two simple base gun propellants, SB1 manufactured in 2005 and SB2 manufactured in 2011 was evaluated by determination of thermal degradation energy (Ea) using different tests such as: auto-ignition, Rapid Screening Device (RSD) and differential scanning calorimetry (DSC). Firstly, the stability was tested using methyl-violet and Bergmann-Junk tests. Then, the auto-ignition technique was used to determine the thermal degradation energy using isothermal and non-isothermal mode. In the isothermal mode, the value of activation energy was investigated using Arrhenius equation whereas in the non-isothermal mode, Kissenger and Ozawa were used. All the tests performed show that the thermal degradation energy of SB1 is lower than that of SB2 which exhibit the existence of a good correlation between them.

Nano differential scanning calorimetry applied to paraffinic crude oils

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Keywords: waxes, petroleum, nanoDSC, WAT, crystal

Brazilian crude oils from the pre-salt layer have high levels of waxes, which are alkanes (linear or branched) with 15 to 75 carbons. Due to the low seabed temperatures (about 4 to 5 °C) [1], the crude oil in the pipeline can be cooled and the waxes can precipitate, leading to unwanted gels, deposition and strong waxy crystal network, which can cause clogs and affects the rheological fluid behavior [2-3]. The wax appearance temperature (WAT) is an important parameter to understand these wax precipitation behaviour because it gives an idea of the petroleum precipitation potential. The WAT can be determined by some techniques such as Near Infrared spectroscopy (NIR), rheology, optical microscopy, and Differential Scanning Calorimetry (DSC). The DSC is the most common and there is currently a variety of equipment available. Micro DSCs are more sensitive to thermal transitions than conventional DSCs, as well as Nano DSCs promises to be more sensitive than micro ones. In this work, measurements were performed using Nano DSC (TA Instruments). 300.0 μL of homogenized and degassed petroleum were heated from room temperature to 80.0 °C, at 2.0 °C/min. Then were held for 15 min at 80.0 °C, following by a cooling step from 80.0 °C to 4.0 °C, at 0.5 °C/min. Kerosene was used as the reference of absence of wax. Through thermal curves (Fig. 1) it is possible to note at least two well-defined exothermic peaks as expected to crude oils. However, a possible third peak at temperatures just below the second peak, it is noted and may represent a population of very short-chain waxes. The WAT values (defined as the intersection point of the baseline and tangent of the inflection point of the first exothermic peak [4]), for P1-P4 were respectively 46.6, 42.1, 46.8 and 53.1 °C. By integrating the area of the exothermic peaks is possible to obtain the total thermal effect of the wax precipitation and thereby the wax precipitated concentration following the Equations from [5]. The precipitated wax content shows 3.1, 2.2, 2.9 and 4.7 wt. % for P1-P4 respectively.

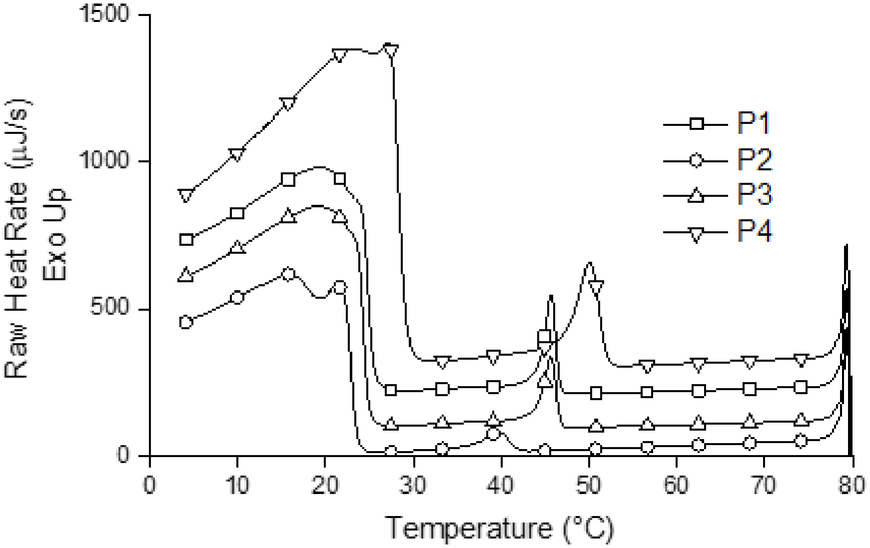

Fig. 1: P1-P4 thermal curves.

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Results of study focusing the thermal and chemical properties of selected short-rotation tree and energy crop species

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Keywords: short-rotation tree species, energy crops, thermal analysis, chemical analysis, pyrolysis

The production of energy from biomass currently has a high political priority, as shown by the European Union target to reach a 20% share of renewable energy by 2020. Growth of short-rotation tree species, short-rotation forests and permanent grasslands for heat production and electricity can make a significant contribution to meeting this goal. At the same time, these activities are an opportunity to diversify agricultural production, and their implementation also supports environmental objectives and greater independence from energy imports. This paper summarizes the state-of-the-art knowledge and research results focusing the application of progressive small-scale analytical methods to assess the fire, thermal, chemical and energy properties of selected short-rotation tree and energy crop species. In the study, there were involved the three species of short-rotation trees: *Paulownia tomentosa*, *Salix viminalis* clone Tora, *Populus x euroamericana* clone MAX 4; and three energy crop species: *Sida hermaphrodita*, *Arundo donax*, *Miscanthus x giganteus.* The paper has form of a compilation of own research results and results achieved by other experts focusing the same issue. Those results were mutually compared, and the conclusions were specified. In the comparison, there were used the data on the spontaneous ignition temperatures, gross calorific values, heating values, ash content, elemental analysis, cellulose, hemicellulose and lignin content, pyrolysis and thermal degradation process as well as the activation energy of the tested wood and crop samples to assess the suitability of individual tree and crop species for energy production purposes.

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Analysis on condensed phase reaction of aqueous hydroxylammonium nitrate using thermal measurements and kinetics

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Keywords: hydroxylammonium nitrate, C80, ab initio calculation, kinetics analysis

Hydroxylammonium nitrate (HAN, $[NH_3OH]^+[NO_3]^-$) has attracted attention as a new generation liquid propellants because it has a good oxygen balance and high performance, and contains no halogen atoms. It is helpful to have information regarding the decomposition and combustion behaviour of propellant ingredients such as HAN when developing comprehensive ignition and combustion models for rocket motor and gas generators employing these materials. The present study focuses on condensed phase reaction of HAN to understand thermal decomposition pathways before combustion. The aim of this study is to analysis on condensed phased reaction of HAN solutions using thermal measurements and kinetics. The thermal behaviour of HAN was measured with micro calorimeter C80 (SETARAM instrumentation) at several constant heating rates. From the measurement results, activation energy and frequency factor of condensed phase reaction of HAN were calculated using kinetics. In a similar way, activation energy and frequency factor were calculated by kinetics from simulation results of thermal decomposition of HAN modelled based on our previous study [1,2]. By comparison of kinetics results between thermal measurements and simulation results, we assumed the important pathway of condensed phase reaction of HAN.

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Investigation on catalytic thermal decomposition for nano metal oxides by thermal analysis

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Keywords: physical chemistry, thermal analysis, nano metal oxide, energetic materials, catalytic thermal decomposition

Possessing a series of new physical and chemical properties, including volume effect and surface effect, ultrafine (nanometer) catalysts has great application in regulating the combustion performance of propellant. Thermal analysis technology has been widely used as a fast and reliable means to study catalysts. Generally characteristic quantity of thermal analysis as decomposition peak temperature, released heat in decomposition process, and the variation of dynamic parameters were measured to characterize catalysts. However, besides their chemical effects, catalysts also show physical effects in mixed systems such as heat dissipation or dilution. The physical effects become more obvious for the catalysts that do not take part in the decomposition process. The physical effects are also more obvious when catalytic thermal decompositions are studied using thermal analysis technology. In addition, the catalytic mode of solid phase catalysts is sometimes "solid-solid", sometimes "liquid-solid" or "gas-solid". In order to make thermal analysis more reliable to study the catalytic effects of nano metal oxides, these physical effects and catalytic modes should be considered. In this paper the catalytic thermal decompositions of HNIW (CL-20), AN and (NG+NC) system by nano metal oxides were studied by PDSC and TG. Characteristic quantity of thermal analysis as initial decomposition temperature, peak temperature and decomposition heat of DSC, peak temperature and mass loss, activity energy, and reaction rate constant were measured to characterized the catalytic effects of these catalysts. In addition, it is found that the phase state (solid, liquid and gas) in the decomposition of the material has a great influence on the catalytic decomposition, the catalytic efficiency of the "liquid-solid" and "gas-solid" catalytic modes is much higher than that of "solid - solid". The results showed Al_2O_3 pairs of HNIW, n-CuO and Fe_2O_3 pairs of NC in the (NG+NC) system all belong to the "solid-solid" catalytic mode, which has a low catalytic efficiency, while n-CuO and n-PbO pairs of AN, n-CuO and Fe_2O_3 pairs of (NG+NC) system all belong to the "liquid-solid" and/or "gas-solid" catalytic mode, which has a high catalytic efficiency. Moreover, the metal oxides are not only a catalyst, but also a "thinner" for some materials capable of self accelerating decomposition, there is heat dissipation or dilution effect such as "negative catalysis" effect. In HNIW/Al_2O_3, (NC+NG)/ n-CuO and (NC+NG)/Fe_2O_3 systems, there is a negative catalytic effect of g-Al_2O_3 on HNIW, n-CuO, g-Fe_2O_3 and n-Fe_2O_3 on NC.

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Isothermal decomposition and kinetic analysis of gun propellants during aging

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Keywords: Isothermal analysis, propellant, kinetics, aging

A comparative study of the isothermal kinetics decomposition of unaged and artificially aged single base gun propellants having different calibres (SBP1 (7.62×39), SBP2 (9×18), SBP3 (9×19)) has been investigated by means of vacuum stability test (VST) [1-3]. Model fitting and model free isothermal methods have been applied to determine the decomposition kinetics of the different sample from VST results [1]. Additionally, a prediction of the safe life time period of the different samples was performed [4]. The obtained results showed that the activation energies obtained by model free method based on VST technique of the different SBP decreased during artificial aging. Furthermore, it was found that there is no significant difference between the activation energies of the unaged samples; hence the calibre type of SBP had no effect on its isothermal kinetic decompositions. Model fitting method proved that the mechanism of thermal decomposition of the different unaged and artificially aged SBP is described by the chemical reaction theory with different model compared to the formers. On the other hand, it was revealed that the safe life of the different samples decreases during accelerated aging, which confirms the harmful effect of aging on the stability of energetic materials.

The present work has demonstrated that VST permits to evaluate the isothermal kinetic decomposition of propellants, revealing that this technique is able to distinguish the differences of the kinetic triplet (Ea, A, and g(α)) of propellants during artificial aging.

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Thermoanalytical studies in the influence of the fuel component on the thermal and catalytic decompositions of HAN based monopropellants

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Keywords: thermoanalytical study, HAN based monopropellant,

New green and high density energy propellant is required to replace the traditional high toxic hydrazine monopropellant. In the past twenty years, hydroxylammonium nitrate (HAN) were reported as the best oxidant of green monopropellant. So the most interesting part is how to choose the fuel component to achieve high energy and fast catalytic decomposition rate. In this work, methanol, ethanol, glycerol and 2-hydroxylethylhydrazinium (HEHN) were chosen as fuel component mixed with aqueous solution of HAN and formed the monopropellants. The thermal decomposition and catalytic decomposition of HAN aqueous solution and these HAN based propellant were investigated. The results showed that in HAN aqueous solutions, the thermal decomposition starts only when water is fully vaporized and HAN is in its liquid state. Methanol, Ethanol in the propellants are vaporized before the decomposition, producing results close to HAN aqueous solution.

Energy conversion and storage

Nitrate hydrates for thermal energy storage

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Keywords: accumulation, phase change materials, supercooling, DSC

An effort to reduce the natural raw material consumption together with the discrepancy between the supply and demand of energy from renewable sources leads to request for long-term energy storage. Phase change materials (PCMs) seem to be suitable candidate for this task and several salt hydrates have been explored extensively [1-3]. However, the large-scale implementation of PCMs into the energy system is still lacking and requires significant improvement of proposed PCMs. The main demands of PCM are: low price, non-toxicity and its stability over thousands of phase change cycles. In the case of phase change cycles (it is the melting-crystallization in the case of salt hydrates) there are two main aspects negatively influencing its repeatability and stability. One of them is the separation of the phases which could be overcome by encapsulation or by addition of filler which sterically prevent from separation [4]. The second aspect is the supercooling – the temperature of the phase change during the charging is higher than the temperature of the phase change during the discharging. The suppression of supercooling is one of the most important steps on the way to practical application and obviously is trying to be solved by addition of nucleating agent [4,5].

In this work the accumulation ability of magnesium nitrate hexahydrate (MNH), cobalt nitrate hexahydrate (CNH) and nickel nitrate hexahydrate (NNH) was studied using differential scanning calorimetry (DSC). All samples were tested by DSC and sets of heating/cooling scans. Moreover, the main thermo-physical properties were analysed using thermoanalytical methods. According to values of the melting temperature of these salts - 89 °C for MNH and ca. 56 °C for CNH and NNH, these materials can be classified as a medium temperature PCMs. Pure salt hydrates were analysed within the four cycles of heating/cooling scan as well as their mixtures with selected improving materials where the heating and cooling rate was 10 K/min in the appropriate temperature range. Based on these few cycles the promising mixtures were tested during 50 cycles of heating/cooling scan. The promising mixtures of nitrate hydrates with additives were further tested in different nitrate/additive mass ratio. The supercooling and phase separation occurred during melting – crystallization cycles were supressed by addition of fillers and nucleation agents (similar to successfully applied into magnesium chloride hexahydrate [6]).

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Effect of salt addition on methene emissions during storage of pig slurry and subsequent biogas production

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Keywords: pig slurry, methane emissions, biogas production, salt addition

Pig slurry (PS) is often held in the liquid form in the farm, waiting for transporting to the final treatment facilities. This storage period lasts for, in general, 1-3 months, in which huge amount of methane (CH_4) can be emitted by the activity of indigenous microbial consortium. To reduce this CH_4 emission, acidification by using sulphuric acid and lowering temperature below 15°C are currently applied [1-2]. However, the acidification has the hazards associated with this strong acid, and the increased presence of hydrogen sulfide in the subsequent biogasification process [3]. And, the decrease of temperature at a high degree seems unrealistic, requiring huge additional energy input, and thermally-isolated cover structure.

In the present work, the new method was tested that adding salt to PS. Salt is easily attainable at a cheap price, and is known to inhibit microbial activity by increasing osmotic pressure. Salt was added to PS to reach the concentration from 1 to 13 g Na^+/L, and then stored at 30°C for 40 d. As storage went on, a cumulative amount of CH_4 emissions was increased, finally recording 8.8 kg CO_2 eq./ton PS, in case of control. However, in salt added cases, it dropped gradually with increasing salt concentration, from 8.3 to 2.9 kg CO_2 eq./ton PS, with less degradation of organic matters. In case of control, organic content was degraded by 40% while it was only 20% at 7 g Na^+/L. Instead of using salt, brackish wastewater (BWW) from desalination plant was also tested. It was found that BWW was more effective in reducing CH_4 emissions, ascribed to the presence of other inhibiting components like heavy metals. The CH_4 emissions was almost dropped by 50% at 5 g Na^+/L. The stored PS was then tested for biogas production. The control sample showed a biological methane potential of 148 mL CH_4/L PS, while the sample stored at 7 g Na^+/L showed 171 mL CH_4/L PS. By reducing CH_4 emissions during storage and increasing the amount of biogas, it can be concluded that salt addition to PS can reduce overall greenhouse gas emissions by 6–54%.

Experimental techniques

For PS storage experiment, a cylindrical tank with a total volume of 1.4 L was used. One litre of PS was added, beside NaCl doses to reach concentrations of 1–13 g Na+/L. On the other hand, certain amounts of brackish wastewater were also tested through being added to 0.8 L of PS to reach final concentrations of 1–9 g Na+/L. Volumes were then adjusted to reach 1 L using distilled water. All tanks were purged with fresh air in order to provide actual storage conditions. Temperature was kept at 30±1 oC using water bath.

For biological methane potential experiments, bottles of 0.6 L working volume were used in continuous mode, while hydraulic retention time (HRT) was fixed to 30 d, corresponding to 2.0–2.8 g COD/L/d of organic loading rate (OLR). Temperature was kept at 37±1 oC, while the agitation speed was 120 rpm.

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Silver modified copper oxide nanostructure for solar thermal energy conversion

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Keywords: CuO microrods; Ag modification; Solar selective absorber; Optical properties; Solar energy conversion

Copper oxide (CuO) nanostructure was prepared using copper nitrate trihydrate, liquid ammonia and sodium hydroxide by varying the pH of the reaction solution. The scanning electron microscopy (SEM) analysis disclosed the formation of one dimensional CuO microrods. The prepared CuO microrods were modified with silver nanoparticles (Ag NPs) of different concentrations and the resultant SEM images disclosed that the one dimensional CuO nanorods are completely submerged or covered by the spherical Ag NPs. The X-ray diffraction (XRD) examination exhibited diffraction peaks at 2θ values of 35.5, 38.7 and 53.5°, which could be attribute to the (0 0 2), (2 0 0) and (0 2 0) diffraction planes, respectively of the end-centered monoclinic CuO and the presence of Ag NPs was confirmed by the appearance of crystalline planes (1 1 0), (2 4 0) and (3 1 1) of cubic Ag correspond to 2θ value of 25.7, 43.6 and 66.6°. The EDAX results obviously revealed that the peaks corresponding to Cu, O and Ag elements are noticed in the spectrum. The reflectance values of the pristine CuO and Ag NPs (20 and 40wt%) modified CuO nanostructures synthesized were 39.72, 26.16 and 22.16%, respectively and their corresponding solar absorptance (α) values were 0.76, 0.78 and 0.81. The results of the study revealed that Ag–CuO nanostructured materials can be employed as spectrally selective absorbers in solar thermal energy conversion systems.

Phase composition, structural, microstructural and electrical properties of sol-gel prepared MeO_x (Me=V, W, Zn) – carbon composites and their possible applications

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The nanocrystalline V_2O_5, WO_3 and ZnO and the composites based on these oxides are considered for different electrochemical applications. The preparation method has a significant influence on material properties such as structure, microstructure, electrochemical properties. The synthesis methods for preparation of nanosize metal oxides are a reverse micelle, rapid foam expansion or hydrothermal synthesis methods which have many drawbacks such as poor repeatability in controlling the size and distribution of synthesized nanoparticles.

One of the possibly better approaches is the use of a sol-gel technique which is a commonly used method for the preparation of metal oxide and thin film coatings. It allows creating materials with different grain sizes dependent on used precursors and conditions of the process (like pH or temperature).

The aim of this work was to determine the possibility of using the sol-gel method to prepare metal oxide-carbon composites (MeO_x/C (Me=V, W, Zn)) with controlled properties in one step process. The influence of processing conditions on physicochemical properties of prepared materials and the performance of Al-ion electrochemical cells prepared from these materials was investigated.

Differential Thermal Analysis and Thermogravimetry combined with Mass Spectrometry (DTA – TG – MS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Electrochemical Impedance Spectroscopy (EIS) and Open Circuit Voltage (OCV) methods were used to optimize the preparation conditions and to investigate the properties of prepared materials. Basing on the results of DTA-TG-MS temperature of the calcination process were established. The results showed that the phase composition, type of structure and the microstructure of the materials depend on the gas atmosphere during the calcination process.

The results of the study of EIS and OCV electrical properties have been interpreted and correlated with the structure and microstructure of the materials. Based on the obtained results the potential application of the materials was proposed and discussed from the point of view of future possible materials modifications.

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Applying of thermal methods for low – carbon practices for decentralized resource utilization

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Keywords: low-carbon practicies, re-carbonization, climate changes

Introducing a well-founded system for sustainable development in the region and mitigating the effects of climate change through low-carbon practices such as: stopping the burning of storms and preventing large-scale forest fires and atmospheric pollution, creating economically justifiable incentives for recovery of waste biomass for regeneration and improvement of the qualities of the main elements of the environment related to one of the main sectors for the region – agriculture, incl. soils, groundwater, guaranteeing soil fertility for the introduction of high-performing productions in farming, livestock and processing industries.

Implementation of municipal low-temperature heating systems with multiplier economic effect – on the one hand reducing the cost of the waste management system to 70% and eliminating the cost of fossil fuels: natural gas, petroleum derivatives, wood pellets, etc.

Exemplary solutions for introducing low-carbon practices for decentralized waste recovery are:

- Utilization of biodegradable and construction waste in the construction of green park urban systems.
- Mobile installations for accelerated decentralized composting of biodegradable waste
- Installations for decentralized urban composting systems:
- Composting of biodegradable hotel waste in a compost reactor
- Waste recovery system to produce carbon-negative heat energy for heating 1000 square meters of built-up area.
- Settlement low-carbon waste disposal sites with regeneration practices.
- Carbon negative practices for flooding forest areas and overcoming the effects of droughts and fires in forestry.
- Carbon negative practices for the restoration of damaged soils (including burned forest land), soil microflora and soil moisture coating.

The above examples have been developed with technical means and are aimed at demonstrating the so-called integrated low-carbon practices through which soil re-carbonization, soil micro-flora development and restoration of soil moisture retention are guaranteed to ensure soil fertility

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Thermal characterization of salt based phase change materials using inverse thermal analysis technique in furnace cooled steel mould

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Keywords: Thermal energy storage, Inverse thermal analysis, solidification, energy balance

Increasing energy demands, shortage of fossil fuels, and growing environmental concern are the reasons responsible for the development of non-conventional and renewable energy sources. Considering the unpredictability of such energies, the energy storage technologies to reduce the mismatch between the energy demands and the supply are extensively researched. Thermal energy storage (TES) technologies focusses on the storage and the uninterrupted dispatch of energy in the form of heat. In TES systems, latent heat thermal energy storage systems (LHTES) using phase change materials (PCM) have higher energy storage density as compared to the sensible heat thermal energy storage systems (SHTES) [1-2]. For implementation of these PCMs in TES systems, thermal characterisation data of these materials needs to be known.

In this study, a new method for the assessment of solidification parameters of PCM salts has been proposed. The thermal history of the salt and the steel mould during solidification of the salt sample is analysed and assessed to obtain the solidification parameters of the PCMs. This method involves the Inverse thermal analysis technique for the determination of the mould-salt interfacial heat flux. This estimated heat flux was further used to calculate the phase change enthalpy of the salt PCMs using calorimetry based energy balance equations. Furnace cooling was adopted to reduce the rate of solidification and radial heat transfer was ensured by maintaining the steel mould dimensions. A solidification range of ±5 of the melting point(T_m) was used for latent heat calculations in this work.

This method is advantageous over other Computer Aided Cooling Curve Analysis (CACCA) methods as it eradicates any drawbacks due to the fitting in baseline calculations and the errors introduced due to the selection of start and end of solidification points. This makes this method more accurate and precise. This method is also devoid of the limitations associated with the conventional characterisation techniques like Differential Scanning Calorimetry (DSC), T-history method such as small sample size, effect of heating and cooling rates, overestimation of super cooling and the usage of reference materials [2].

Pure Salt PCMs such as KNO_3 and $NaNO_3$ were used for validation of this method. The solidification parameters such as rate of cooling, start and end of solidification points, time taken for solidification and latent heat of the PCMs were determined. The values of the solidification parameters obtained by this method were in close agreement with the data reported in the literature.

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Facile Synthesis of Diverse Copper Oxide Nanostructures for Solar Thermal Energy Conversion

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Keywords: Facile preparation; CuO nanostructures; Oxidizing agent; Solar energy conversion, Optical properties

Copper oxide (CuO) nanostructures were synthesized using $Cu(NO_3)_2 \cdot 3H_2O$ through a simple wet chemical oxidation method by sodium hydroxide (NaOH) as an oxidizing agent. The scanning electron microscopy (SEM) analysis revealed the formation of diverse CuO nanostructures as a consequence of varying the concentration of NaOH in the reaction medium. The X-ray diffraction (XRD) examination disclosed the formation of end-centered monoclinic CuO as evident from the diffraction peaks at 2θ values corresponding to the diffraction planes. The existence of cubic phase Cu_2O was confirmed by the presence of diffraction peak at 2θ value of 61.5°, corresponding to the (0 2 2) diffraction plane. The energy-dispersive X-ray spectroscopy (EDAX) analysis of the elements confirmed that the formed polycrystalline CuO nanostructures were pristine in nature. The UV-Vis-NIR reflectance value of the CuO samples prepared using different concentrations of NaOH exhibited reliable solar absorptance (α) value, which were in accordance with their respective reflectance values.

A study on high temperature oxidation resistance of undoped and doped higher manganese silicide powders prepared by pack cementation

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Keywords: higher manganese silicides, thermoelectric powders, pack cementation, oxidation resistance

High oxidation resistance and the possibility to form oxides that impede the oxidation propagation are highly desirable properties for a thermoelectric material. Especially up to the temperature where its maximum efficiency has been reported, it is important for it to remain unaffected in order to perform to its highest potential. The oxidation behaviour essentially depends on chemical stability and the physical properties of the oxidation products. Higher manganese silicides (HMS), with the general formula $MnSi_{\sim 1.7}$, are considered among the alternative thermoelectric materials with the most attractive features. These compounds exhibit good thermoelectric performance, low-cost, non-toxicity, mechanical and chemical stability, and high oxidation resistance. They have demonstrated a figure of merit ZT~0.7 for the undoped material [1], further enhanced to a value up to 1 by using various dopants [2]. To date, numerous methods have been applied for the preparation of $MnSi_{1.7}$. The objective of this work is a study of the high temperature oxidation of $MnSi_{1.7}$ powders synthesized by the pack cementation process. The powders were undoped or enhanced with the suitable dopant. The samples synthesized at different experimental conditions were exposed to high temperature air environment using a thermogravimetric setup (TGA). Non-isothermal oxidation tests up to 1200 ^{o}C and isothermal tests at selected temperatures were carried out. The structure determination and phase identification of the samples, before and after oxidation, were performed by X-Ray diffraction analysis (XRD). The morphology and the chemical composition were examined using a Scanning Electron Microscope (SEM) equipped with EDS analyser.

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Thermal performances of *n*-alkylammonium tetrachlorocuprate eutectoid mixtures as phase change materials

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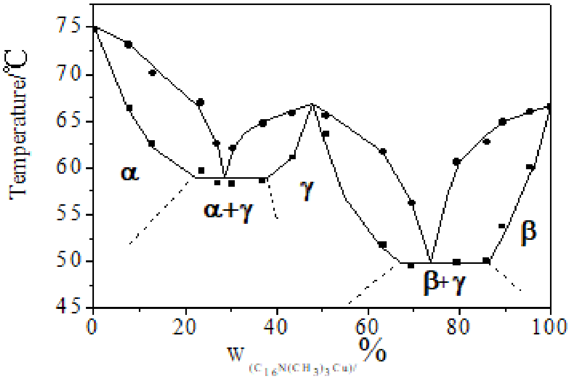
Keywords: Bis(*n*-alkyammonium) tetrahelometallates; Phase change materials; Differential scanning calorimetry; Eutectoid temperature; Phase diagram

The thermotropic phase-transition compounds *n*-alkylammonium tetrachlorocobaltate $[n\text{-}C_nH_{2n+1}\ N(CH_3)_3]_2CuCl_4$ (n = 16, 18) and a series of their binary mixtures were prepared by solution reflux at 353 K from ethanol solutions. Binary-mixture $[C_{16}H_{33}N(CH_3)_3]_2CuCl_4$-$[C_{18}H_{37}N(CH_3)_3]_2CuCl_4$systems were characterized over the entire composition range using differential scanning calorimetry and X-ray diffraction. The phase diagram constructed from the experimental results indicated one stable intermediate phase, $[C_{16}H_{33}N(CH_3)_3][C_{18}H_{37}N(CH_3)_3]CuCl_4$, at a mass fraction w_{C16Cu} = 48.51%, two invariant three-phase equilibria, and two eutectoid temperatures, which are assigned to e_1 at (331 ± 1) K, for the eutectoid point with w_{C16Cu}=28.50%, and e_2 at (3223 ± 1) K, for the eutectoid point with w_{C16Cu} = 73.86%. These three clear solid-solution ranges are á-phase on the left, â-phase on the right, and ã-phase in the middle of the phase diagram. The $[n\text{-}C_nH_{2n+1}N(CH_3)_3]_2CuCl_4$ binary-mixture systems as phase change materials have phase-transition temperatures T in the range 340–370 K, and transition enthalpies ΔH in the range 61.61–106.30 J g^{-1}, between two polymorphic crystal forms.



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Synthesis and thermal properties of starch/ polyethylene glycol copolymers for thermal energy storage

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Keywords: polyethylene glycol, starch, phase change material, solid-solid phase change

Nowadays, the limited reserves of fossil fuels make the effective utilization of energy to be a general concern. Phase change materials (PCMs), which are capable of storing and releasing thermal energy during phase change procedure, provide an elegant and feasible solution to improve energy utilization in many sectors[1]. Polyethylene glycol (PEG) has good thermal stability and chemical properties. It has high enthalpy of phase change, no super cooling and no toxicity[2]. It has been widely studied and applied in the field of phase change energy storage. However, as it is a solid-liquid phase change material, how to prevent its leakage in the phase change process by physical or chemical methods has become the focus of current research.

In this work, a novel composite phase change material has been synthesized by chemical grafting method, in which polyethylene glycol as phase change molecular chain, starch as molecular skeleton and 4, 4'- two phenyl methane diisocyanate as crosslinking agent were used in this work. The chemical structure, phase transformation performance, thermal stability, micromorphology and crystal structure of the composite phase change materials were investigated by differential scanning calorimetry, thermogravimetry, fourier transform infrared, scanning electronic microscopy and X-ray diffraction respectively. The results prove that the novel composite phase change material has been synthesized successfully by using fourier transform infrared, scanning electronic microscopy and X-ray diffraction analysis. And thermal analysis results show that the phase transition process of the composite phase change material displays as the behaviour of solid-solid phase change material, that is there is not leakage as it occurs phase change. Meanwhile, its phase transition temperature is in the range of 306–329 K; and its phase transition enthalpy is from 89 to 110 J/g. This kind of composite material is non-toxic and degradable, and is expected to be used as phase change materials for potential application.

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Exergy, Experimental thermodynamics

Construction of lanthanide complexes based on 2,6-dimethylbenzoic acid and 5,5’-dimethyl-2,2’-bipyridine: Supramolecular structures, thermodynamic properties and luminescence

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Keywords: Lanthanide complexes, Crystal structure, Thermodynamic properties, Heat capacity, Luminescence property

By using conventional solution method, two novel binuclear lanthanide complexes, [Eu(2,6-DMBA)3(5,5’-DM-2,2’-biby)]2(1), and [Sm(2,6-DMBA)3(5,5’-DM-2,2’-biby)]2(2) (2,6-DMBA = 2,6-dimethylbenzoate, 5,5’-DM-2,2’-biby = 5,5’-dimethy-2,2’-bipyridine), have been synthesized at room temperature. The two complexes are characterized by element analysis, single-crystal X-ray diffraction analyses and powder X-ray. The single-crystal analyses results indicate they are isomorphous in the monoclinic space group of P2(1)c. The binuclear complexes 1 and 2 are linked to form 1D, 2D supramolecular structures through the same C-H···O hydrogen bonding interactions. The thermal decomposition processes of these complexes are investigated by TG-DSC/FTIR technology and the FTIR spectra of the escaped gas also are measured. What's more, in a temperature range from 295.15 to 410.15 K, heat capacities of the title complexes are measured by a DSC instrument, which indicates that there no take place phase transition in this range,and the heat capacity values of the complexes gradually increases with rising temperature. Not noly that, the thermodynamic functions values (HT-H298.15K) and (ST-S298.15K) of the complexes 1 and 2 are calculated according to the fitted polynomial equations and the thermodynamic equation.

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Differences of isothermal calorimetry and liquid culture of synchronous conditions for saccharomyces cerevisiae fermentation

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Keywords: Saccharomyces cerevisiae, bioethanol, fermentation, isothermal calorimetry, bioenergy

We focused on *Saccharomyces cerevisiae* (*S. cerevisiae*) fermentation, using sugar substrate to turn into bioethanol fermentation, by comparing isothermal calorimetry and actual liquid fermentation, to determine the differences of adjustment substrate, culture temperature, and time for *S. cerevisiae* fermentation. Meanwhile, we compared the effects of different fermentation temperature of 25, 31, and 37 °C, the various glucose and fructose substrate concentration of 2, 4, and 8 mass%, and the suitable fermentation time for *S. cerevisiae* fermentation under synchronous culture environments. It is an innovative research topic to find favorable conditions for bioethanol production by comparing isothermal calorimetry and actual liquid fermentation, and then to adjust the suitable fermentation conditions of culture medium, time, and temperature. We acquired the various glucose and fructose substrate concentrations, the substrate time, and the substrate temperature affecting the concentration of bioethanol produced under synchronous culture conditions. Overall, the results of this research can be provided as a reference for bioenergy and wine processing.

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Solid-liquid phase diagrams of binary systems containing chlorobenzene and chlorocyclohexane with n-alkanes: experimental data and correlations.

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Experimental solid – liquid phase diagrams [1] were determined for binary systems consisting in chlorobenzene and chlorocyclohexane with n-hexane, n-heptane, n-octane, n-nonane and n-decane.

DISQUAC group contribution model [2] [3] was applied to predict the studied solid – liquid phase diagrams.

The interaction parameters (gad/RT) and (had/RT) between alkane group (a) and chlorine group (d) in chlorocyclohexane are the same as those used in 1 – chloroalkanes + n-alkanes binary systems.

The interaction parameters (gad/RT) and (had/RT) between alkane group (a) and chlorine group (d) in chlorobenzene are adjusted on experimental excess Gibbs energy and excess enthalpy of chlorobenzene + n-alkane binary system.

Calculated solid-liquid phase diagrams are in good agreements with experimental data.

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Efficienecy improvement in solar cogeneration using microchannel heat exchangers

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Keywords: Cogeneration, Thermodynamic efficiency, microchannel heat exchangers, solar energy

Combined cooling, Heat and Power (CCHP) is defined as sequential generation of two or more forms of energy from a single thermal source. The two major thermodynamic cycles available for cogeneration are the Kalina cycle and the Goswami cycle. Both Kalina and Goswami cycles use ammonia-water binary mixture as a working fluid to produce heat, power and cooling (cooling water). This binary mixture has been chosen to control the boiling point and hence the ratios between the three outputs can be varied. Goswami cycle consist of 3 heat exchangers. This work addresses the improvement in efficiency of Goswami cycle using two approaches: a) Optimization of ammonia composition in the vapor entering the turbine b) Replacing the inefficient conventional heat exchangers with microchannel heat exchangers whose number of transfer units (NTU) is greater than 7. A microchannel heat exchanger consisting of 500 micron wide channels has been fabricated and tested for its heat transfer capabilities. The heat transfer coefficient was found to be more that 5000 W/($m^{2.}$ K) for sensible heat exchange between ammonia-water mixture to water and the same was found to 8000 W/(m^2. K) for the boiling and condensation heat transfer. The performance of microchannel heat exchangers in Goswami was compared against the conventional heat exchangers. The performance was compared through simulation performed using Aspen HYSYS. It was found that the Goswami cycle with microchannel heat exchangers is 26% more efficient when compared to that of conventional heat exchangers. Further, the cooling water temperature (Cooling effect in Goswami Cycle) can be as low as 6oC.

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Design of a velocity-coupled modified T-burner for aluminized propellants

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Keywords: combustion instabilities, velocity coupling, T-burner, solid propellants, solid rocket motors

This paper describes the design of a modified T-burner that measures the velocity coupling response of metalized solid propellants. Additionally, this device can quantify the conventional pressure coupling response. It is composed of a center-vented tube with an inner diameter of 70mm and an assembly of many short cylindrical burners. The desired frequency is set by the number of the small burners used. This architecture allows for the placement of the propellant sample at many locations along the combustor. Two propellant drivers are mounted at both ends of the T-burner to provide a continuous parallel flow of hot gases throughout the chamber. A pulser system is used to excite the desired longitudinal standing acoustic wave within the burner.

The velocity coupling response is determined to be approximately 19.5, under a mean pressure of 6.5MPa and for a fundamental frequency of 175Hz, which is almost an order of magnitude greater than the pressure coupling response (≈4). These values also indicated that the velocity coupling is a significant mechanism of the combustion instabilities raised in solid motor rockets.

Inhibiting effects oF Ionic liquids of different ANions ON coal spontaneous combustion of lignite

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Keywords: coal, severe disaster, ionic liquid, different anion, key indicator

From the previous study, spontaneous combustion of coal sporadically happened, and caused a severe disaster. Now, the problems of coal spontaneous combustion are still existing. In addition, ionic liquids (ILs) were used as the inhibitor in numerous applications. Actually, the effects of IL for treating coal to inhibit the spontaneous combustion properties had been explored in recent years. However, the research only focused on ionic liquids of different cations, and rarely discussed the effects of different anions on coal spontaneous combustion. For this study, thermogravimetry, Fourier-transform infrared spectroscopy, and kinetic models were employed to probe the inhibiting effects of ILs of different anions. The key thermal parameters could be obtained, including onset (T0) and peak temperatures (Tp), apparent activation energy (Ea), mass loss derivative (DTG), and reaction duration. Furthermore, the functional groups, and the key gaseous productions could be measured to identify the key indicator when the treated coal combusted. Finally, this study provides a better choice of the ILs which could substantially inhibit the spontaneous combustion of coal.

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Prediction and assessment of multiple tubes of fireworks by thermokinetics model

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Keywords: consumer fireworks, pyrotechnic effects, fly up type, thermokinetic parameters, thermal safety model

In consumer fireworks, chemicals have various functions that create an energetic reaction with colored light, smoke, heat, and sound to achieve pyrotechnic effects. These firework mixtures have elevated sensitivity to explosive degradation on ignition, temperature, impact, friction, and electrostatic stimulation. Approximately 95% of fireworks are imported from China by ocean shipment, taking four days to a week in Taiwan. The multiple tubes (fly up type) of the fireworks are used by most consumers. The aim of the project was to predict and assess the nth order reaction, autocatalytic reaction, and thermokinetic parameters from a thermal safety model for fireworks and pyrotechnic compositions. The study showed which reaction intensity of the propellant was palliated as water was added. The wetted propellant was not easily self-reactive in any case. SADT of wetted propellant was more than 100.0 °C for five package sizes. Moreover, it is important to avoid water infiltration, which increases the heat amount and peak intensity of the propellant and consequently increases the risk for an explosion.

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Extraction of o-cresol and acetonitrile from water using an ionic liquid

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Keywords: liquid/liquid extraction, choline bis(trifluoromethylsulfonyl)imide ionic liquid, O-cresol, acetonitrile.

The pollution of water in its various areas of existence (oceans, seas, rivers, rivers and groundwater) in the whole world in general and third world countries in particular is a fact. This pollution is either of industrial origin, agriculture or household. The industry generates organic and inorganic pollutants such as hydrocarbons, pharmaceuticals and heavy metals. Agriculture generates pesticides, herbicides and household waste such as sanitary products and detergents. The protection and the depollution of the water of these various effluents is a challenge to be taken up by the scientists in general and the chemists in particular. The present study, which is part of this objective, consists of extracting ortho-cresol and acetonitrile from the aqueous solution using an ionic liquid (IL) Choline Bis (trifluoromethylsulfonyl) imide [Choline] [NTf2]. This study consists of the determination experimentally of the liquid-liquid equilibrium diagram of the two ternary systems {water (1) + [Choline] [NTf2] (2) + O-cresol or acetonitrile (3)} at atmospheric pressure and at T=295.15 K. These two diagrams were obtained experimentally by analyzing the tie-line data of the aqueous phase and the ionic liquid phase by Gas Chromatography. The consistency and reliability of the experimental data were ascertained and validated by the Othmer-Tobias correlation. The values of the distribution and selectivity coefficients determined from the experimental data indicate that [Choline] [NTf2] is a suitable ionic liquid for the extraction of these two organic compounds from the aqueous solution.

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Comment on "Experimental analysis of gas explosions at non-atmospheric initial conditions in cylindrical vessel" by Cammarota et al., Process Saf. Environ. Prot. 2010, 88: 241–249

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Keywords: Gas explosion, Deflagration index, Cylindrical vessel, Length to diameter ratio

In this comment we point out that the commented paper maybe exist some mistake in the deduce process of the deflagration index formula, and the difference between the deflagration index formula of the spherical and cylindrical vessel are also simply discussed. We recommend that the authors should update the deflagration index equation so that the explosion characteristics can be probably described much more accurately.

Acknowledgments

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Fuels, biofuels

Mixing of solid refused fuel particles in a bubbling fluidized bed: experimental and numerical studies

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Keywords: mixing, SRF, fluidized bed, fluidization velocity, bed-particles-size

In this work, experimental and theoretical studies have been carried out to investigate the mixing of Solid-Refused Fuel (SRF) particles in a bubbling fluidized bed. The investigations include the effect of fluidization velocity ratio and the bed-particles-size. The experiments were performed on a pilot-scale cold-flow fluidized bed. The bed material (sand) and the SRF particles have average particles-diameters of (dpm = 654,810 and 1110μm < sand >, and dpm = 3520μm < SRF >). The SRF axial concentration was measured using the Bed-Frozen Method at three axial locations within the bed, namely the bottom, the middle, and the top. The theoretical CFD model is based on the finite volume Eulerian-Eulerian approach. The CFD model showed overall acceptable agreement with the experimental data of this heterogeneous system when assuming the SRF particles as disks of sphericity ratio of 0.23. The results showed that in the bed body (middle) regime, the relative mass fraction of SRF was exhibiting a rising trend at low fluidization velocities (u/umf = 1.2 ~ 1.6) and over this range, the SRF concentration stabilizes around a saturation value of ~ 33.5%. Increasing the inert bed particles size was found increasing the SRF concentration in the middle and the top layers of the bed.

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Degradation of polypropylene using silica based meso-macroporous material evaluated by TG

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Keywords: Meso-Macroporous Silica, Polyethylene, Thermogravimetry

Polypropylene (PP) is the most widely used thermoplastic, ranging from the production of bottles, food packaging, soil sieves, tree shelters and sewage pipes. Due to its high demand and low biodegradability, the formation of solid plastic waste becomes a threatening issue to the environment and thus, scientific researches towards recycling polypropylene and plastic in general is desirable so we can find new ways to recycle this solid residue. PP can be recycled through thermal decomposition with set parameters such as temperature, heating rate, time and the use of catalysts. While the standard recycle method for plastics is efficient, chemical recycling is a very attractive alternative because it can produce petrochemical products and low-chain hydrocarbons. The catalytic cracking of polymers over traditional zeolites is limited by the low accessibility to its micropores, which have diameters smaller than 1 nm. To overcome these constraints, meso-macroporous solids, with pore diameter higher than 50 nm are very interesting materials because they combine the high catalytic activity in the mesoporous with the accessibility of the macropores. These new materials are composed by a non-crystalline silicate or aluminossilicate phases combined with the well ordered porosities, and are attracting attention of researchers due to their potential applications in catalysis for processing bulky molecules, such as polymers1. The aim of the present work, is the synthesis and characterization of Meso-Macroporous Silica (MMS) materials, and application for thermocatalytic pyrolysis of polypropylene (PP). The thermogravimetry was used for determination of the activation energy, by using multiple heating rate kinetic model, proposed by Ozawa-Flynn-Wall (OFW). The activation energies versus degree of conversion of PP with and without catalyst were studied. The catalyst was synthesized by the hydrothermal method, from a sodium silicate solution containing n-decane as organic template, hydrochloric acid and acid as solvent, following the procedure previously reported 2. The obtained material was calcined and characterized by X-ray diffraction, BET surface area by nitrogen adsorption and scanning electron microscopy. The thermogravimetry analysis of PP with the meso-macroporous silica was performed in order to determine its activation energy (Ea) relative to polymer decomposition process. The PP used was obtained from a commercial plastic bottle. The TG analysis was carried out on a thermobalance SDT-Q600 from TA instruments, from room temperature up to 600 °C, under nitrogen atmosphere flowing at 60 mL/min, at heating rates of 5; 10 and 20 °C/min. Through TG/DTG analysis, it was observed that the PP degradation occurs in the temperature range of 373–505 °C. From the Ozawa-Flynn-Wall kinetic model, the values of Ea for PP was ca. 221 kJ/mol, that reduced to 192 kJ/mol with the presence of the solid catalyst. The observed decreasing of the Ea is due to the presence of active sites in the mesoporos channels combined with accessibility of the macroporous.

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Evaluation of the thermal and oxidative properties of diesel/biodiesel blends with high pressure DSC

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Keywords: Thermal and oxidative stability, Blends diesel/biodiesel, Biofuels

Due to the environmental problems that have emerged in recent decades, such as air pollution and the emission of greenhouse gases, it is increasingly being sought to replace the use of fossil fuels with other renewable energy sources. In Brazil, road diesel is the most commonly used petroleum-derived fuel since the matrix of transport of the products produced in the country is based on the road network. According to the National Agency for Petroleum, Natural Gas and Biofuels, in 2017 Brazil was the seventh country among the largest consumers of oil products, with a forecast of 19% increase in national demand between 2016 and 2026. In this way, the use of biofuels should be increased so that the country can meet the targets agreed at the United Nations Conference on Climate Change (COP21) held in Paris in 2015. In this context, biodiesel presents itself as a source of clean energy capable of totally or partially replacing diesel without any detriment to the performance of vehicles operating with diesel cycle, since no technical modifications are necessary for conventional engines for their use, obtaining specific consumption, power, and similar yield. Mixtures of diesel with high concentrations of soy biodiesel (5 to 50% v/v) have been investigated to evaluate the technical feasibility of their use in diesel cycle engines, in terms of thermal and oxidative stability properties. The results of combined techniques of oxidative stability, high-pressure DSC and Rancimat, as well as cetane number and calorific value determination were used to verify the effect of biodiesel content increase in the mixtures. For both techniques, it was observed the dramatical reduction of the thermal and oxidative stability with the addition of biodiesel in concentrations above 10%, caused by the formation of peroxides, and subsequently the formation of organic acids. These results indicate the use of antioxidant additives for higher biodiesel levels; otherwise, the oxidation compounds should degrade the quality of the product and impair vehicle performance, causing problems associated with corrosion and clogging, in various mechanical systems.

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Experimental study of low-rank coals using simultaneous TG-DTA techniques under air conditions and radiation level characterization

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Keywords: Low-rank coals; TG-DTA; Oxidative characteristics, Ignition; Kinetics parameters; Radioactivity

Thermal analysis of two low-rank (lignite) coal samples from different Serbia basins ("Kolubara" and "Nikola Tesla A" power plants) was studied to identify ignition temperatures in the process of oxidation and spontaneous combustion. All experiments were carried out under non-isothermal linear regime of heating, from 30 up to 1000 oC at the different heating rates (β = 10, 20 and 30 oC min-1). The reaction regions, peak, the burn-out temperatures, the mass loss, and heat effects were determined for each heating rate from TG-DTG and DTA curves appearance. Based on the obtained thermal analysis data and subsequent comparative analysis of estimated results, the difference in the oxidative characteristics of investigated coals was discussed. Friedman, Kissinger-Akahira-Sunose and Ozawa-Flynn-Wall methods were applied to determine the activation energies (E) and the logarithm of pre-exponential factors (logA) behaviours of coals decomposition in an air atmosphere. The model-free methods were used to indicate the global kinetics of decomposition process. Possible differences in isoconversional nature of these coals during their heating up to the high temperatures were discussed. Coal contains natural radionuclides and in combustion leads to their enrichment in ashes. Data on the content of natural occurring radionuclides in coal samples from coal-burning thermal power plants were discussed using results obtained from gamma spectrometry analysis.

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Effect of salt addition on methene emissions during storage of pig slurry and subsequent biogas production

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Keywords: pig slurry, methane emissions, biogas production, salt addition

Pig slurry (PS) is often held in the liquid form in the farm, waiting for transporting to the final treatment facilities. This storage period lasts for, in general, 1-3 months, in which huge amount of methane (CH4) can be emitted by the activity of indigenous microbial consortium. To reduce this CH4 emission, acidification by using sulphuric acid and lowering temperature below 15oC are currently applied [1-2]. However, the acidification has the hazards associated with this strong acid, and the increased presence of hydrogen sulfide in the subsequent biogasification process [3]. And, the decrease of temperature at a high degree seems unrealistic, requiring huge additional energy input, and thermally-isolated cover structure.

In the present work, the new method was tested that adding salt to PS. Salt is easily attainable at a cheap price, and is known to inhibit microbial activity by increasing osmotic pressure. Salt was added to PS to reach the concentration from 1 to 13 g Na+/L, and then stored at 30oC for 40 d. As storage went on, a cumulative amount of CH4 emissions was increased, finally recording 8.8 kg CO2 eq./ton PS, in case of control. However, in salt added cases, it dropped gradually with increasing salt concentration, from 8.3 to 2.9 kg CO2 eq./ton PS, with less degradation of organic matters. In case of control, organic content was degraded by 40% while it was only 20% at 7 g Na+/L. Instead of using salt, brackish wastewater (BWW) from desalination plant was also tested. It was found that BWW was more effective in reducing CH4 emissions, ascribed to the presence of other inhibiting components like heavy metals. The CH4 emissions was almost dropped by 50% at 5 g Na+/L. The stored PS was then tested for biogas production. The control sample showed a biological methane potential of 148 mL CH4/L PS, while the sample stored at 7 g Na+/L showed 171 mL CH4/L PS. By reducing CH4 emissions during storage and increasing the amount of biogas, it can be concluded that salt addition to PS can reduce overall greenhouse gas emissions by 6–54%.

Experimental techniques

For PS storage experiment, a cylindrical tank with a total volume of 1.4 L was used. One litre of PS was added, beside NaCl doses to reach concentrations of 1–13 g Na+/L. On the other hand, certain amounts of brackish wastewater were also tested through being added to 0.8 L of PS to reach final concentrations of 1–9 g Na+/L. Volumes were then adjusted to reach 1 L using distilled water. All tanks were purged with fresh air in order to provide actual storage conditions. Temperature was kept at 30±1 oC using water bath.

For biological methane potential experiments, bottles of 0.6 L working volume were used in continuous mode, while hydraulic retention time (HRT) was fixed to 30 d, corresponding to 2.0-2.8 g COD/L/d of organic loading rate (OLR). Temperature was kept at 37±1 oC, while the agitation speed was 120 rpm.

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Rsm optimization of pistacia lentiscus oil transesterification assisted by micro wave

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Keywords: biodiesel, transesterification, pistacia lentiscus, optimization

In spite of the biodiesel great benefits in the performance improvement and pollutant emissions reduction of a diesel engine, the large application of this biofuel remains restrictive due to economic consideration. This study focuses on the energy efficiency improvement of the Pistacia Lentiscus (PL) oil transesterification conducted under micro wave irradiations instead of the conventional mechanical stirring. Several reaction time values 1–5 min, temperatures from 20–40 °C and KOH catalyst amounts in the range 0.5–1.5 wt.% are investigated. The reaction yield is modeled using response surface methodology combined with full factorial design in order to reduce the number of experimental test cases. The results show that the optimum conditions are obtained for a reaction temperature of 40°C, catalyst amount of 1.04 wt.% and a reaction time of 5 min. These conditions lead to reach a conversion rate around 97% and a considerable energy saving during the micro wave process compared to mechanical conventional stirring. The characterization of PL biodiesel shows that the physicochemical properties are similar to those of conventional diesel fuel and in agreement with the international requirements.

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Impact of humidity and oxygen concentration on thermophysical properties of coal

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Keywords: LFA457, thermal diffusivity, specific heat capacity, thermal conductivity, spontaneous combustion

To determine the influence of the gas environment with different humidity and different oxygen concentration, the LFA457 laser flashing instrument was used to test the thermophysical parameters of coal under different oxygen concentration and humidity. The results indicated that at the same temperature and humidity, with the increased oxygen concentration, the thermal diffusivity of coal increased gradually, the specific heat capacity decreased slightly, and the thermal conductivity did not change significantly. At the same temperature and oxygen concentration, with the increase of gas humidity, the thermal diffusivity of the coal slightly lessened, the specific heat capacity gradually rose, and the thermal conductivity decreased. At the same oxygen concentration and humidity, with the increase of temperature, the thermal diffusivity and specific heat capacity of coal was basically unchanged, and the thermal conductivity did not significantly vary. Furthermore, compared with air humidity, the oxygen concentration had little impact on the thermophysical properties of coal, but humidity had a great effect. Gas humidity is one of the vital factors to be considered in heat conduction for coal spontaneous combustion.

The effect of [bmim][bf4] on low-temperature oxidation thermal characteristics of coal under different oxygen concentrations

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Keywords: low-temperature oxidation; thermal characteristics of coal; C80 microcalorimeter; LFA457 laser-flasher; different oxygen concentrations

Coal can conduct low-temperature oxidation to release heat. The thermal production from low-temperature oxidation of coal is easy to accumulate since coal is a poor thermal conductor. The consequence of this phenomenon is generating coal spontaneous combustion (CSC). Our aim was to study the effect of ionic liquid [BMIM][BF_4] on the low-temperature oxidation heat characteristics of coal with different metamorphic degrees and the effect of oxygen concentration on low-temperature oxidation heat characteristics of [BMIM][BF_4] treated coal. The C80 microcalorimeter and the LFA457 laser-flasher were used to test three different metamorphic degree coal samples. The results indicated that [BMIM][BF_4] had outstanding inhibitory effects on the heat release characteristics parameters (heat release, heat release rate and exothermic characteristic temperatures) and heat transfer characteristic parameters (thermal diffusivity, specific heat capacity and thermal conductivity) of low-temperature oxidation of coal. The best inhibitory effect of [BMIM][BF_4] on coal samples was lignite. The inhibition of [BMIM][BF_4] on the low-temperature oxidation heat characteristics of coal was enhanced with the decrease of oxygen concentration. The drop in oxygen concentration further reduced the heat release and heat release rate of coal low-temperature oxidation, and undermined the ability of coal to transfer heat owing to the temperature difference.

Geosciences and minerals

Heat transfer mechanism in oil saturated rock materials at high temperatures

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Keywords: heat -transfer mechanism, heat capacity, laser-flash method, thermal conductivity, thermal diffusivity.

To evaluate the geothermal energy generation systems we have to predict the amount of heat present and the rate at which it can be extracted. These are the prime factors affecting the economics of any recovery process. These two factors (amounts of heat and recovery rate) in turn depend on basic physical properties of the reservoir rocks and fluids containing within them. The rate of heat extraction depends on the thermal conductivity, $Q = -\lambda(T) grad\ T$, and the fluids flow characteristics, while amounts of recovery heat depends on heat-capacity of reservoir rocks, $Q = (1\text{-}\varphi)\rho C_P\ T$, where φ is the porosity. In the present work the laser-flash LFA [1] and differential scanning calorimeter (DSC 204 F1) [2] techniques were employed on a heavy oil saturated rock sample for accurate measurements of the thermal diffusivity and heat-capacity over a temperature range from (294 to 774) K.. The density of the sample at room temperature is 2210 kg·m-3 and the porosity was 17.1 %. The sample of the present study comes from Russian Oil Field. The uncertainties of the thermal diffusivity and heat-capacity measurements are within 3 % and 1 %, respectively. The measured values of the thermal diffusivity and heat-capacity were used to calculate thermal conductivity of the rock sample as $\lambda = a\rho C_P$, where ρ =2210 kg·m-3 is the sample density. The effect of temperature and various physical and chemical processes, such as thermal decomposition of pore oils (chemical reactions) occurred in the sample during the heating in distinct temperature ranges, was studied. The significant effect of oil thermal decomposition (sample thermal stress) on the measured values of heat-capacity of rock sample at high temperatures (above 680 K) was experimentally found. We experimentally observed temperature maximum of the heat-capacity of the sample under study in distinct temperature ranges around 380 K (low-temperature range) and at 680 K (high-temperature range). We showed how the decomposition (chemical reactions) of the pore fluid can affect the measured properties (heat-capacity and thermal diffusivity). We attribute these maximums to the dehydration (evolution the volatile matter, devolatilazation) and aromatization of the carbon (thermal decomposition), which are known to occur under heat treatment, that tend to increase the heat-capacity.

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Non-isothermal decomposition kinetics of hydrated volcanic glass (pitchstone)

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Keywords: volcanic glass, dehydration kinetics, isoconversional, Arrhenius equation, pitchstone, perlite

Pitchstone constitutes secondary hydrated amorphous volcanic glass; its water content ranges between 5 and 10 % and is chemically bound to its index forming molecular water and OH groups. Sophisticated thermal treatment of hydrated volcanic glass (expansion) allows the production of frothy material that is used in many applications, due to its low density and significant thermal insulating properties. Due to considerable water content of pitchstone, expansion process cannot be applied to raw pitchstone, and a preliminary selective dehydration step is needed to selectively remove the excessive water content and maximize the material expansion performance.

Dehydration kinetics of fine pitchstone samples have been studied through thermogravimetric analysis in air atmosphere under 4 different heating rates (2, 5, 10, 20 °C) and heating temperature between 25 and 800 °C. Dehydration extends to temperature between 200 and 600 °C, and weight loss rates maximize between 257 and 306 °C. Under these conditions pitchstone samples weight loss range between 7.04 and 7.40 % wt. and is solely attributed to water species release. Apparent activation energy (Ea) of pitchstone dehydration has been calculated through rate and integral isoconversional methods. The calculated Ea values of both methods are similar throughout the conversion degree, exhibiting mean value of 109.8 kJ/mol at conversion between 0 and 0.7. Determination of pre-exponential factor and reaction model was performed through masterplots method, and it was found that pitchstone dehydration obeys the Fn model, with n value between 5 and 6. The model predictions are in agreement with the experimental data.

Thermal characteristics of asphaltenes to evaluate evolutionary processes in the oil reservoir

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Keywords: asphaltenes, kerogen, oil, thermal characteristics, differential scanning calorimetry

It is considered that oil asphaltenes are small structural fragments of kerogen not transformed into oil and therefore can contain information about the geochemical history of oil [1]. In a simplified form, the asphaltene molecule can be represented as a three-dimensional macromolecule consisting of a condensed polyaromatic core with lateral aliphatic substituents. In current concept is that asphaltenes in oil are presented in the form of supramolecular assemblies of different hierarchies (very stable nanoaggregates or clusters of nanoaggregates) [2]. Due to the network structure the asphaltene aggregates can occlude, and due to the developed surface – adsorb the compounds with certain size and structure from the ambient medium (maltenes) [3]. The qualitative composition of compounds occluded in asphaltene aggregates provides information about protopetroleum, the quantity of occluded and adsorbed compounds in asphaltene aggregates, as well as the structure of asphaltene aggregates will indicate the degree of transformation of asphaltenes and, accordingly, allow to evaluate the evolutionary processes in the oil reservoir. In the present work in order to study the degree of asphaltene transformation a comparative analysis of the thermal characteristics of asphaltenes from both oils of different age deposits and bitumoid of domanic deposits of the Bavly oil field of the Republic of Tatarstan (Russia) was carried out. According to the thermal analysis data, by analogy with [4], for asphaltenes the index F, characterizing the share of occluded and/or adsorbed compounds in asphaltene aggregates, and the index P, characterizing the share of peripheral substituents relative to condensed naphthene-aromatic structures in asphaltene molecules, were calculated. It was shown that bitumoid asphaltenes in comparison with oil asphaltenes contained more the occluded and/or adsorbed oil components that indicated their looser structure. In oil asphaltenes, the share of occluded and/or adsorbed compounds was less, and the share of condensed naphthene-aromatic structures increased with increasing deposit age. It was shown that the removal of occluded and/or adsorbed compounds from asphaltenes leaded to the transformation of asphaltenes to carbene-carboidic compounds. The data obtained allows us to propose that in transforming kerogen to oil, the compaction of asphaltene aggregates occurs, the proportion of occluded and/or adsorbed compounds in them decreases. The same trend is observed for oil asphaltenes with increasing age of deposit: the degree of transformation of asphaltene aggregates increases and the share of occluded compounds in them decreases.

Acknowledgments
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Impact of high energy milled activation on the thermal properties of Bulgarian and Estonian natural apatites

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Keywords: High energy milled activation, Carbonate apatite, Quartz, Isomorphic substitution, Thermal analysis

We investigated high energy milled (HEM) samples of natural phosphorites from Bulgarian and Estonian deposits. The activation was performed via planetary mill with Cr-Ni grinders with a diameter of 20 mm. This method is an alternative for environmental protection eliminating the disadvantages of conventional methods, namely release of gaseous and solid technogenic products.

The aim of the study is to determine the changes in the structure, to follow the solid state transitions, the isomorphic substitutions in the anionic sub-lattice in the structure of main mineral apatite in the samples from Bulgaria and Estonia under the influence of HEM activation. It is also interesting to investigate the influence of HEM on structural-phase transformations on the structure of impurities minerals - free calcite/dolomite, pyrite, quartz, as well as to assess of their influence on the thermal behavior of main mineral apatite.

The effect of HEM is monitored by the using of a complex of analytical methods, such as chemical analysis, specific surface area (SSA), X-ray powder diffraction (XRD), Fourier transformed infrared (FTIR) measurements and thermal analysis (TG/DTG-DSC) coupled with Pfeiffer Omnistar Mass Spectrometer.

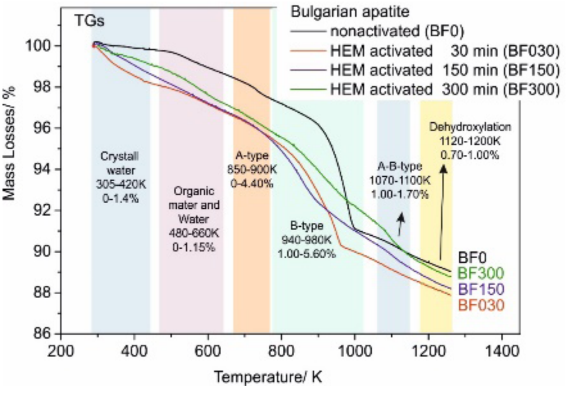

Fig.1 TG curves of thermal decomposition of non-activated and HEM activated samples of Bulgarian apatite

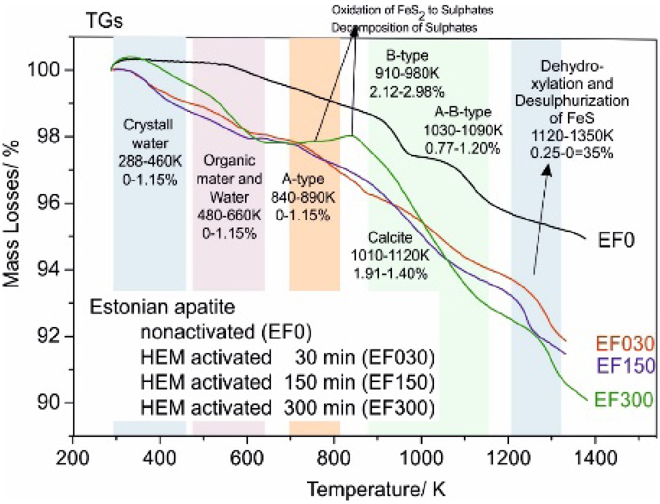

Fig.2 TG curves of thermal decomposition of non-activated and HEM activated samples of Estonian apatite

The study on activation effect shows that the mechanical activation impacts at the micro-level is following: (i) change the strength of chemical bond; (ii) deformation of polyhedrons; (iii) smaller size of crystallites with increased degree of structural defects leading to meta-stable phosphorite with increased dispersity.

The obtained results show correlation in the behavior of the studied samples in regards of their quartz content and bonded or non-bonded carbonate ions. After HEM activation of the raw samples, the A-and A-B type carbonate-apatite are formed. The new isomorphic phases (A-and A-B type carbonate-apatite) are decarbonized at temperature of about 780-850 K and 1050-1100 K. In the presence of quartz, the decomposition temperature for carbonate ions in A-site is increased. In addition, the moisture and higher quartz content in the samples leads to shift of dehydroxylation temperature.

Acknowledgments

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Thermal analysis and FTIR spectroscopy of syntetic clay mineral mixtures

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Keywords: clay minerals, thermal analysis, infrared spectroscopy

Clay minerals belong among the most widespread minerals in the earth's crust rock system. As the products of the weathering processes, they form an essential component of sedimentary rocks. The nature and content of clay minerals significantly influences the properties and behaviour of rocks and then entire rock massifs. Despite the rapid development of new analytical techniques, accurate identification of these minerals in the rocks is rather difficult and often inaccurate. The main reason is their varying chemical composition and frequent structural defects. A small particle size of clay minerals (below 0.002 mm) prevents the use of conventional optical microscopes. Also, the fact that these minerals occur in nature in the form of mixtures bring problems associated with the identification of present individual clay minerals. Mixed structures consist of at least two types of basic structural units, alternate regularly or irregularly in a direction perpendicular to the plane of the layers. First, they are mixed structures with permanent properties, which are considered as separate mineral species for example rectorite, kulkeit and several other rare minerals. Second and more frequent is the irregular rotation of structural units with very variable percentage, for example mixed structures of illite-smectite, chlorite-vermiculite, chlorite- smectite, illite-kaolinite, kaolinite-chlorite etc.

One of the promising combination of analytical methods suitable for the characterization of clay mineral mixtures are combination of thermal analysis and FTIR spectroscopy. In this work, the assay mixtures were prepared from the common clay minerals with fraction of particle size less than 5 μm varying by a proportional representation of the base constituents of the mixture ranging from 10% to 90%. The mixtures thus prepared should at least partly simulate natural mixed clay structures. The aim was to find characteristic peaks on DTA curves as well as absorption bands in IR spectra suitable for the identification of clay minerals in mixtures and at the same time to determine the minimum content of detectable minerals.

Acknowledgments

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Thermoanalytical Investigation on Natural Clayey Materials, Sands and Volcanic Ashes

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Keywords: natural clays, thermogravimetry, differential scanning calorimetry

A thorough thermoanalytical characterisation on a wide set of natural clayey materials, sands and volcanic ashes from Sicily (mainly from the Mount Etna area) has been carried out.

Thermogravimetric curves have been recorded in a variety of experimental conditions. A TA Instruments thermobalance model Q5000IR equipped with an FTIR Agilent Technologies spectrophotometer model Cary 640 for evolved gas analysis (EGA) was employed. TG measurements were performed at rate of 10 or 20 °C/min from 30 to 950 °C under air or nitrogen (25 mL min^{-1}). TG-FTIR measurements were performed at a rate of 20 °C/min in the same temperature range under nitrogen flow (90 mL min^{-1}), from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

TG-DSC analysis on selected samples representative of each group of materials was performed from 30 to 950 °C at a rate of 10°C/min by using a Netzsch STA 449 Jupiter instrument under nitrogen flow (25 mL min^{-1}).

Three or four decomposition steps (at about 60°C, 250°C, 500° and 700°C) were detected for natural clays according to their geographical origin. Compositional analysis of the gases evolved in correspondence with the most significant degradation steps of each thermogram has been carried out by FT–IR spectrometry.

The combined approach enabled us to discriminate between hygroscopic or zeolitic water and structurally bonded water. In combination with gas–volumetric measurements of the loss of CO_2, a precise determination of bonded water was also possible.

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Heat transfer

Heat exchanger using the corona wind for heat recovery from hot gas

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Keywords: corona wind, gas engine, exhaust gas, heat exchanger, heat recovery

In recent years, biogas has become an important source of renewable energy. Biogas can be used instead of fossil fuels in internal combustion engines to generate electric power, thereby reducing greenhouse gas emissions. Exhaust gas, mainly comprising carbon dioxide, is produced from engines at temperatures of up to 300 °C [1]. The emission of such hot gases not only wastes energy but also leads to thermal pollution of the environment. In fact, 60–70% of the primary energy is lost as waste heat; in internal combustion engines, ~33% is lost in exhaust gas [2]. Therefore, combined heat and power units that can perform multiple roles efficiently and safely offer an important mechanism for energy cascade utilization in power generation engine system.

The heat exchanger is the main component used for heat recovery; it is used to transfer heat between hot and cold fluids. Many studies have tried to improve heat transfer efficiency of the heat exchanger performance in an internal combustion engine. In this study, we suggest the use of corona wind for heat recovery from exhaust gas. Corona wind is an emerging technology that can use electro-fluid energy conversion, where bulk air motion is induced by a corona discharge between electrodes such as a wire and a plate.

This study develops a new type of heat exchanger with tungsten wires to produce a corona wind. Experimental data are presented for the velocity and temperature of the corona flow from wires to parallel electrodes with respect to the applied voltage and power. Additionally, a gas engine power generation system is manufactured, and its power generation efficiency is tested according to the fuel gas volume fraction between methane and carbon dioxide. Furthermore, an exhaust gas heat recovery system is fabricated using the proposed heat exchanger. A prototype of the corona wind heat exchanger is manufactured, and its enhanced heat recovery efficiency is tested with the gas engine. The corona wind heat exchanger operates well under the available exhaust gas conditions; it increases the temperature of 1 L/min water flow by 45 °C by recovering 2 kW of heat energy from the exhaust gas. The total power production efficiency was increased from 29% to 47%. The results confirm that the proposed corona wind heat exchanger can be applied to the gas engines to greatly enhance their heat recovery efficiency.

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Inorganic materials

Replacement of fluorine in mould powders: influence on the crystallization kinetics

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Keywords: mould fluxes, crystallization, kinetics, differential thermal analysis

Mould fluxes (mould powders or casting powders) are used in the continuous casting process of steel. These powders melt when are poured onto the liquid steel, and then penetrate between the steel shell and the mould wall. In this stage, the heat transfer must be controlled to prevent several problems because it is responsible to bring an adequate heat extraction from the steel solidified shell to the copper mould [1]. In order to control the heat extraction, the formation of crystals at temperatures between 500–900°C must be taken into account. For this reason, it is important to know the kinetics of crystallization of these fluxes in such temperature range. At present, commercial mould powders contain fluorine (F) in their chemical composition. However, the presence of F produces gas emissions that can cause corrosion problems in the plant, water acidification in refrigeration circuits and damage to personnel health. Therefore, the replacement of fluorine by less harmful constituents such as B_2O_3, Na_2O, TiO_2 and Li_2O [2-4] is a research topic of industrial interest.

In the present work mould powders were prepared using different raw materials. One powder was fluorine-containing and the others were free-F. The total fluorine content (approx. 10 wt%) was replaced by different percentages of boron, sodium and lithium oxides. Fluorspar (CaF_2), borax anhydrous ($Na_2B_4O_7$), and lithium carbonate (Li_2CO_3) were employed as source of fluorine, boron, and lithium, respectively. These powders were milling during 2 hours, then were melted at 1300°C and finally fast cooled onto a stainless steel plate. The amorphous solid layers as obtained were milling to produce glass powders which were tested by DTA at different heating rates: 5, 10, and 15°C/min. Several non-isothermal methods (Kissinger, Augis-Bennet, Ozawa, Cheng) were applied to study their kinetics of crystallization. From these models, different parameters associated to crystal growth, such as the activation energy (Ec), the frequency factor (ν) and the nucleation rate (kc), were determined. Crystallographic phases and crystal size distribution were determined by X-ray diffraction and microscopic observation techniques.

Regardless of the models used, it is observed that the replacement of F by B_2O_3 increases the values of the activation energy Ec and decreases the reaction rate kc. The sample containing B_2O_3 and Li_2O showed the lowest crystallization peak (between 585°C and 625°C). This flux also presented the lowest values of Ec (≈ 180 kJ/mol), νc (≈ 4x109 s-1) and kc (between 0.06 s-1 and 0.18 s-1). It is noted that the fluorine-containing powder presented a higher crystallization rate kc (between 0.15 and 0.43 s-1) than the free-fluorine powders.

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The effect of dopants on synthesis and thermal stability of $BiFeO_3$ pigments

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Keywords: perovskite, ferrite, brown pigments, thermal stability

Inorganic pigments are black, white, coloured or fluorescent powder materials, whose main role is the colouring of the matrix into which they are incorporated. Pigments are insoluble in the matrix and do not react chemically or physically with matrix. These materials consist of a stable crystal host lattice doped by transition metal cations which act as chromophore cations. The chromophores are the source of colour properties of the materials. A classification of inorganic pigments can be done in various ways, for example by the colour, crystal structure or thermal stability. The pigment with the highest degree of heat stability and chemical resistance can be predominantly used for colouring ceramic glazes, ceramic bodies, porcelain enamels, glass enamels, roofing granules, and other coatings of high temperature performance requirements.

Presented work deals with preparation of pigments based on structure of $BiFeO_3$. Bismuth iron oxide is technologically and scientifically very interesting well known multiferroic material, but its potential use as an inorganic pigment is limited by its low thermal stability. Pure $BiFeO_3$ can be prepared by solid state reaction of Bi_2O_3 and Fe_2O_3 mixture at 850°C for short time that is 5–10 min. Upon further isothermal annealing at the same temperature for 2 h, the $BiFeO_3$ started to decompose into $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$ [1]. During material preparation, Bi undergoes easy evaporation and generates bismuth vacancies. These defects can be overcome by the partial substitution of Bi^{3+} by rare earth ions or by Sr^{2+} ions [2]. The substitution has also positive effect on thermal stability of samples. The substitution of 20 mol % of Bi^{3+} by Sr^{2+} ions shifted its thermal stability to 1130 °C and powder with composition $Bi_{0.65}Sr_{0.35}FeO_{3-}\delta$ has thermal stability higher than 1161 °C. An increasing range of substitution is also connected with change of the pigment colour from reddish-brown to orange-brown and back to reddish-brown [3].

Therefore, the main aim of our study is focused on increasing the thermal stability of brown pigments based on structure of $BiFeO_{3.}$ The powders $Sr_{0.2}Bi_{0.8-x}In_xFeO_{3-}\delta$ and $Sr_{0.2}Bi_{0.8-x}Ln_xFeO_{3-}\delta$ were synthetized by solid state reaction in the range of substitution (x= 0–0.3) and the effect of dopants on the thermal stability and colour parameters of powders was evaluated. The reactions taking place during the pigment formation were studied by simultaneous TG–DTA analysis (STA 449C Jupiter; NETZSCH, Germany). Powder specimens (225–300 mg) in corundum crucibles were heated up to a temperature of 1000 °C with heating rate 10 $°C.min^{-1}$ in air. α-Al_2O_3 was used as a reference material. The thermal stability of final pigments was tested using a heating microscope EM201-15 (Hesse Instruments, Germany). The samples in form of tablets were gradually heated from room temperature to 1200 °C and a change of sample's areas were detected. The heating rate was 10 $°C.min^{-1}$. The phase composition of the pigments was studied by X-ray diffraction analysis using a MiniFlex 600

(Rigaku, Japan) diffractometer. The colour properties of the powders applied into matrix were objectively evaluated by measuring of spectral reflectance using a spectrophotometer ColourQuerst XE (HunterLab, USA). The measurement conditions were the following: an illuminant D65 and measuring geometry d/8°. For description of colour, the CIE L*a*b* colour space (also referred as CIELAB) was used.

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Conventional and inverse barocaloric effects around triple points in ferroelastics $(NH_4)_3NbOF_6$ and $(NH_4)_3TiOF_5$

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Keywords: heat capacity, entropy, high pressure, barocaloric effect, solid refrigerants

Barocaloric effect (BCE) associated with the reversible change in the entropy/temperature, $\Delta S_{BCE}/\Delta T_{AD}$, under pressure variation under the isothermal/adiabatic conditions is characteristic for substances of different physical origin. The values of extensive, $\Delta S_{BCE}= -\int(\partial V/\partial T)_p dp$, and intensive, $\Delta T_{AD}= -\int(T/C_p)(\partial V/\partial T)_p dp$, BCE strongly depend on a coefficient of the volume thermal expansion $\beta=V^{-1}(\partial V/\partial T)_p$. Solids under usual conditions show as a rule rather low β compared to gaseous refrigerants used in the traditional vapor – compression systems. However, near phase transitions the $(\partial V/\partial T)_p$ of solids can often vary by several orders of magnitude. In such a case ΔS_{BCE} and ΔT_{AD} can reach very large magnitudes [1]. Moreover, when heated through a point of the phase transition, the structural distortions may be accompanied by either increase or decrease in the unit cell volume. Thus, BCE can be either conventional, $(\partial V/\partial T)_p>0$, associated with decrease in ΔS_{BCE} and increase in ΔT_{AD} under applying pressure or inverse, $(\partial V/\partial T)_p<0$, $\Delta S_{BCE}>0$ and $\Delta T_{AD}<0$.

In the present work, we investigated barocaloric properties of the two ferroelastic oxyfluorides $(NH_4)_3NbOF_6$ and $(NH_4)_3TiOF_5$. At ambient pressure, niobate undergoes two structural phase transitions in a very narrow temperature range: T_1=260 K and T_2=262 K, whereas titanate shows only one phase transition at T_0=264.7 K. Entropy of the structural transformations was found very large, in $(NH_4)_3NbOF_6$ $\Delta S_1+\Delta S_2$=(8.5+30.3) J/mol·K and in $(NH_4)_3TiOF_5$ ΔS_0=18.1 J/mol·K, and independent on pressure, at least up to 0.5 GPa. The $T-p$ phase diagrams show triple points and crystal phases induced by high pressure.

The dependences of $\Delta T_{AD}(T,p)$ and $\Delta S_{BCE}(T,p)$ were determined analyzing data on the heat capacity, the T-p phase diagrams and the dependences of entropy of the phase transitions on temperature and pressure. It was found that the maximum values of the extensive and intensive BCE can be realized at rather low pressure (0.1–0.3 GPa). BCE observed around the triple points demonstrate options worthy of attention and are comparable with the caloric parameters of the known solid refrigerants of different origin [1,2]. In both compounds, the conversion from the conventional BCE to the inverse is observed in very narrow temperature range and followed by gigantic change of both $|\Delta S_{BCE}|$ and $|\Delta T_{AD}|$.

The possibility of improving the barocaloric properties by changing the chemical pressure is discussed.

Acknowledgements

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The role of oxoanions in the thermal decomposition of $[Agpy_4]XO_4.4[Agpy_2XO_4]$ (X=Mn, Cl) double salt complexes having tetrahedral $Agpy_4$ cation and three-coordinated $((\kappa1^N\text{-py})_2Ag\text{-}\kappa^1\text{-}OXO_3$ units

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Keywords: oxoanions, pyridine, silver, double salt complexes, TGA, DSC, TGA-MS

Due to its mild oxidizing properties, '[Agpy2]MnO4' is widely used in organic chemistry as oxidizer [1,2]. Its synthesis, structure and possible derivatives are also in focus of research [3,4]. The structure of the analogue [Agpy2]ClO4 compound and its derivatives are also known yet [5,6], but their thermal characteristics were not examined. In a detailed study is discussed the synthesis of [Agpy2]MnO4, its derivatives and analogues in pure form [7]. Since for further application of the compounds their thermal stability is crucial, we have continued the previous work with examination of thermoanalytical properties of [Agpy4] XO4·4[Agpy2XO4] (X=Mn and Cl). Thermal decomposition routes of complexes were compared to determine the role of anions and the presence of hydrogen bonds between the pyridine ring hydrogens on the thermal reaction pathway. The thermal characteristic of the perchlorate complex were studied with TG, DSC and evolved gas analysis methods under inert atmosphere and oxygen, to compare the results with the data given for the isomorphic permanganate complex. The role of the strength of hydrogen bonds between the XO4 anions and pyridine hydrogens and the oxidation potential of the XO4 anions toward the pyridine ring was detected in initiating and appearance of redox reactions between the ligand (py) and XO4 anions. The role of atmospheric oxygen in the decomposition processes (as surplus oxygen source to initiate ignition of pyridine ring) has already been discussed.

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Thermal study of organic–inorganic layered perovskite-like bi-containing titanate

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Keywords: perovskites, organic-inorganic hybrids, thermolysis, simultaneous thermal analysis

Hybrid organic-inorganic compounds based on layered perovskite-like oxides is a new promising class of materials which properties could be tailored by targeted modification of both organic and inorganic parts. Preparation of such materials is recently focused on a stepwise approaches including subsequent hydrothermal and microwave-assisted hydrothermal intercalation and grafting reactions that lead to the formation of bulk hybrid compounds followed by their exfoliation into 2D organically modified nanosheets. [1] Such hybrid compounds and nanosheets are considered as perspective materials exhibiting photocatalytic, catalytic, ferroelectric, and luminescent properties. Although, the thermal behaviour of such hybrids have not been yet widely studied, their application might be strongly dependent on their thermal stability. Additionally, in some cases, the thermolysis of thermally stable organic-inorganic compounds may lead to the modification of organic part without its complete elimination resulting in the formation of carbon layer in the interlayer space of inorganic host. Such approach, for example, may be used for the synthesis of carbon-modified visible-light photocatalysts.[2]

In the present work we report the results on the study of thermal stability of organic-inorganic materials based on the protonated form of layered perovskite like oxide H2K0.5Bi2.5Ti4O13·H2O belonging to Ruddlesden-Popper phases. N-amines namely, methylamine, n-butyl and n-octylamine has been used as organic modifiers. Amine-intercalated compounds have been obtained by facile room temperature and hydrothermal-assisted reactions between amines and inorganic hosts. The phase purity of all of the obtained samples was controlled by XRD analysis and their composition was characterized by simultaneous thermal analysis (TG + DSC) coupled with mass-spectrometry (MS), FTIR spectroscopy and CHN analysis. The advantages of STA analysis coupled with MS for quantitative analysis of organic hybrids are considered in comparison with CHN analysis. The influence of length of carbon chain in amines on the conditions required for the formation of hybrids and their thermal stability has been studied. It was found that n-butylamine intercalated compound could be easily obtained by facile treatment of the host protonated form by n-butylamine at room temperature for a relatively short time (24h), while the formation of methylamine hybrid requires longer reaction times (up to two weeks) or hydrothermal heating. In case of n-octylamine the preliminarily n-butylamine intercalated HKBT is required as a precursor. Although, n-butylamine hybrid could be easily obtained at room temperature, it demonstrated a higher thermal stability comparing to methylamine-intercalated compound. In this regard, it has been used for a further preparation of carbon/nitrogen-containing composites via thermolysis. Thermolysis was carried out by calcination of the organic-inorganic hybrid at different temperatures, chosen in accordance with results of TG. The structural and composition changes during thermolysis were studied by XRD and CHN analysis. It was found that the complete decomposition of the sample occurs at temperatures above 800ºC, leading the formation of Bi4Ti3O12 and Bi2Ti2O7 after calcination at 1000ºC, and the layered structure is maintained at temperatures below 700ºC. CHN analysis showed a gradual decrease of the hydrogen content in the sample with its complete removal at 350ºC, suggesting the formation of carbon/nitrogen-containing layer.

Acknowledgments

Scientific research was performed at the Research Park of St. Petersburg State University: Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre. This work was supported by RFBR (grant 18-03-00915).

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Synthesis and calorimetric study of lantanide orthotantalates

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Keywords: DSC, adiabatic calorimetry, phase transition

Orthotantalates of rare earth elements LnTaO4 possess high chemical and thermal stability. These important refractory compounds, in both unalloyed and doped forms, show many promising applications due to their ionic conductivity, photoelectric activity, and luminescence properties. Such practical applications as photocatalysis for H2 production, photodecomposition of contaminants, electrolytes in solid oxide fuel cells (SOFCs) and phosphors for light emitting diodes (LEDs) are currently being studied.

The chemical stability of rare earth orthotantalates is beneficial for applications, but complicates the development of new materials. Traditional methods of synthesis require solid state annealing at high temperatures up to 1600°C with multiple grinding. In this work, lanthanide orthotantalates were synthesized by the method of reverse precipitation of water-alcohol solutions of components in ammonia, followed by dehydration and stepwise annealing of the obtained precipitate.

The synthesis features were studied using simultaneous thermal analysis (DSC/TGA) and X-ray diffraction. Dehydration of the precursors occurred when heated up to the temperature of interaction of the components, which was 600–950°C, depending on the lanthanide. The interaction of the components was characterized by a pronounced exothermic effect.

The orthotantalates of the most of rare-earth elements LnTaO4 crystallize in two monoclinic fergusonite-type polymorphic modifications – the stable M-structure (I2/a, Z=4) and the metastable M’-phase (P2/a, Z=2) [1]. Heating of precursors to 1000°C leads to formation of nano-scale M’-phase, which transforms to bulk M -phase only after the long-term calcination at 1200°C. And only calcination at 1400°C leads to the complete and irreversible formation of a stable single-phase monoclinic M-structure of LnTaO4 [2], which, possibly, is carried out with the participation of the high-temperature tetragonal modification.

Measurements of heat capacity M-YTaO4, M`-YTaO4 was performed using adiabatic calorimetry and differential scanning calorimetry in the temperature range of 7–1350 K. Detail study of M`- and M-YTaO4 heat capacities showed that the difference between heat capacities of Cp(M)-Cp(M’) is insignificant, but it goes beyond the confidence interval and reaches the highest relative values in the region of the lowest temperatures.

Thermodynamic functions were calculated based on fitted Cp(T) curves.

Acknowledgments

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Study of the thermal behavior of the aceclofenac complexes of samarium and europium

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Keywords: thermal analysis, lanthanides, aceclofenac

Research on molecules with pharmacological actions containing metal ions are widespread in several areas of research, such as chemistry, biology and biochemistry. The use of rare earth metals, are of great scientific importance, since these metals can be used in various types of materials. [1,2]. The objective of this work was to characterize thermally the acrylofenac metalloprices of samarium and aceclofenac of europium. The TG-DSC analyzes of the samarium complex indicate that the first mass loss occurs in the temperature range of 50–115 °C, with an endothermic peak at 110 °C. The anhydrous samarium compound is stable at 195 °C and above this temperature the thermal decomposition occurs in two consecutive stages, with a temperature range between 195–300 °C and no thermal event in the second step, attributed to the thermal decomposition and pyrolysis of the compounds, although the mass losses are still observed up to 1000 °C. The TG-DSC curves of the europium compound indicate that the first mass loss occurs between 50–115 °C, with endothermic peaks at 95 °C and 110 °C. The anhydrous compound presented thermal stability up to 195 ºC and above this temperature the thermal decomposition occurred in two consecutive stages, between 195–300 ºC (fast process) and 300–950 ºC (slow process), with losses of 45.77% and 36. 15%. It was concluded that the TG-DSC analysis allowed to characterize the thermal behavior of the synthesized compound, as well as to establish its stoichiometry. It has been determined that the europium and samarium compounds have 2.5 hydration waters, and three metal binders. Simultaneous TG-DSC curves provided information on the thermal behavior of these compounds (dehydration, stability, thermal decomposition steps) and show that the decomposition of the compounds occurs in four (Sm) and five (Eu) stages. The DSC curves allowed to quantify the energies involved in the processes of dehydration, oxidation and transformations of physical phenomena.

Acknowledgments

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Gel combustion synthesis of ferrite nanopowders

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Keywords: ferrite, gel combustion method, thermal analysis, ceramics

Ferrites are currently considered the most promising materials for creating spintronic devices. The possibility of their practical use largely depends on synthesis conditions and crystallization temperature [1].

The gel auto combustion method is one of the best methods for producing ferrite powders. This method eliminates the need for long-term high-temperature annealing used to crystallize the powder. This is possible due to the short reaction time of the gel auto-combustion. The conditions of this stage have a significant impact on the quality of the ferrite powder. This paper presents the results of studying the effect of various organic complexing agents (glycine, citric acid, starch, urea, polyvinyl alcohol, etc.) on the structure and thermal behavior of the organometallic gel, and the structure and properties of the final product.

Synchronous thermal analysis of the gels and powders was used as the main research method. Using the example of magnetic semiconductor gallium-substituted magnesium ferrite, the thermal behaviour of the gels in a stream of air and argon in the range of 25–600ºC was studied. It has been established that at temperatures of ~135–165ºC there is a sharp mass loss, accompanied by a significant exothermic effect. This is associated with the burning of gels. It is evident that this temperature range characterizes the initial combustion of the gels, but the actual combustion temperature of the sample is much higher.

To determine the combustion temperature of the gel, a mathematical approach was developed based on the results of DSC measurements (differential scanning calorimetry), Gibbs energy changes and reaction entropy. The actual temperature of combustion of the gel is shown to be significantly lower than the adiabatic one, that is usually used in the calculations of thermodynamic parameters of the combustion process.

On the basis of the presented method for producing powdered ferrites, promising materials for designing a new class of magnetoelectronic devices can be created.

The revealed patterns "synthesis conditions – features of the precursor – powder quality" play an important role in the development of the technology for producing functional ferrite-based ceramic materials.

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Synthesis and properties of oxygen-conducting phases LixLa5-xMo3O16.5-yFx (x = 0–1.6)

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Keywords: LiLa4Mo3O15F, Nd5Mo3O16, fluorite-like compounds, oxygen conductivity, phase transitions

In the 1970s, the Ln_2O_3- $Mo(WO_3)$ (Ln = La-Tb) systems were intensively studied with the aim of finding double molybdates and tungstates in them. It is known that in a number of Ln_2O_3-MoO_3 systems there are compounds with the composition 5:6 ($Ln_5Mo_3O_{16}$) with the fluorite-like structure [1].

Fluorite-like $Ln_5Mo_3O_{16+\delta}$ ($0 \le \delta \le 0.5$) compounds have mixed oxygen-electronic conductivity, with a magnitude of the order of 10^{-2} S/cm at 800 °C [2, 3]. A study by Faurie [4] showed that when one rare earth element is replaced by an alkaline element and one oxygen by fluorine, $MeLn_4Mo_3O_{15}F$ compounds (Me = Li, K, Na) are formed with the safekeeping of the fluorite structure. However, the properties of these compounds changed dramatically, a phase transition occurred in the region of which the conductivity increased abruptly [5]. The reason for this phenomenon has not yet been explained.

In this work, we synthesized the solid solutions in $La_5Mo_3O_{16.5}$ - LiF join of the LiF - La_2O_3 - MoO_3 ternary system in air. We study the conditions of solid state synthesis, polymorphism and the properties of $Li_xLa_{5-x}Mo_3O_{16.5-y}F_x$ (x = 0–1.6) compounds using X-ray, DSC and measuring the electrophysical properties, in particular, their piezoelectric response was investigated.

Wide region of $Li_xLa_{5-x}Mo_3O_{16.5-y}F_x$ solid solutions (x = 0–1.6) with a cubic fluorite-like structure have been found in $La_5Mo_3O_{16.5}$ - LiF join. It should be noted that successful synthesis of these compounds significantly depends on the temperature and time of synthesis. The upper limit of time and temperature is strongly limited by the volatility of fluorine, which, according to thermogravimetry, evaporates from the compounds above 750–800 °C, and then the $Li_xLa_{5-x}Mo_3O_{16.5-y}F_x$ compounds decompose. The optimum synthesis temperature was in the region of 600–700 °C.

Polymorphism and properties of $Li_xLa_{5-x}Mo_3O_{16.5-y}F_x$ samples with high fluorine content are of particular interest. At a temperature of about 580 °C, a reversible phase transition is observed for these samples, which is accompanied by DSC anomalies, a peak of the dielectric constant (Fig. 1) and an intense jump in conductivity by two orders of magnitude. These samples also demonstrate significant piezoelectric response, which may indicate the ferroelectric nature of the phase transition. XRD study did not reveal any difference between XRD diffraction patterns of pure $La_5Mo_3O_{16}$ and $Li_xLa_{5-x}Mo_3O_{16.5-y}F_x$. However, it can be assumed, taking into account the above mentioned changes in physical properties, that upon doping, the cubic structure is distorted, although only slightly.

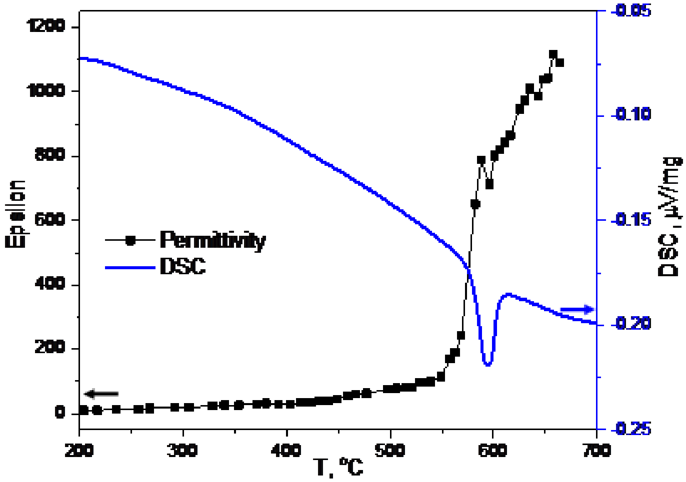

Figure 1. DSC curve and permittivity for the $Li_{1.2}La_{3.8}Mo_3O_{14.7}F_{1.2}$ compound.

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CO_2 mineralization BY burnt oil shale and cement bypass dust: effect of operating temperature and pre-treatment

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Keywords: CCS, Mineralization, Alkaline wastes, TGA

Mineralization of gaseous CO_2 into thermodynamically stable carbonates is a Carbon Capture and Storage (CCS) method, which could become viable in case the industrial wastes are utilized as sorbents [1]. In this context, current study concentrates on the abundantly available power and cement plant ashes, burnt oil shale (BOS) and cement bypass dust (CBPD) which is characterized by a high content of portlandite and lime [2]. The aim of the present study is two-fold. Firstly, it investigates alkaline wastes BOS and CBPD as sorbents in CO_2 mineralization process at different operating temperatures. Secondly, it attempts to quantify the effects of pre-treatment (e.g. hydration and fineness *via* grinding) on CO_2 uptake. Series of parallel experiments were carried out under iso-thermal heating conditions (50ml/min, 100%CO_2) by using thermogravimetric analyzer (TGA) and rotating tube-furnace for larger scale tests. Kinetic analyses of the carbonation process were performed based on experimental measurements. The changes in sample composition and physical characteristics were followed *via* chemical analysis, XRD, FTIR and BET methods. According to the results, effect of milling was found to be not as significant as hydration. Temperature raise and hydration increase the reactivity of all samples resulting in different extents of CO_2 capture for each sample (Fig.1a). There are high initial carbonation rates for all samples yet the CO_2 uptake levels tend to decrease with time. According to the FTIR analysis (Fig.1b), the intensity of portlandite peaks (3640 cm^{-1}) decreases and carbonates (872, 1417 cm^{-1}) increases after carbonation process. Ca-bearing silicates (1123 cm^{-1}) play a role in carbonation reactions of CBPD as their intensities also decrease. The results indicate that CBPD has a higher trapping potential for CO_2 compared to the selected types of BOS samples which could be more effectively used as binders after hydration treatment.

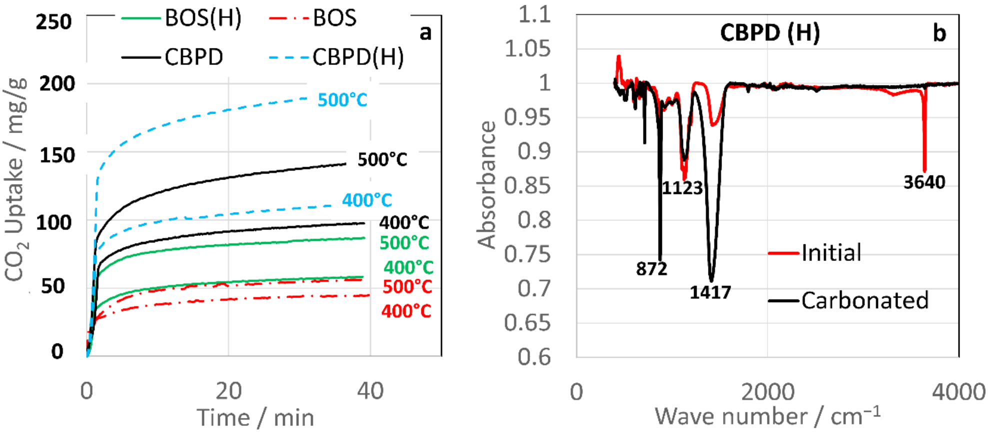

Figure 1. (a) Selected CO_2 uptake curves of BOS and CBPD (H-hydrated) (b) FTIR spectra of CBPD

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Preparation of analcime via hydrothermal treatment

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Keywords: analcime, metakaolin, hydrothermal curing, zeolites

Analcime $NaAl(Si_2O_6)\bullet(H_2O)$ is one of microporous zeolites with irregular channels that occurs in nature. In dependence on the conditions of its formation and present impurities, it can possess different crystallographic systems (cubic, tetragonal, orthorhombic, monoclinic or triclinic). It is used as an absorbent in the treatment of wastewater or, in the case of the metals-modified analcime, also as heterogeneous catalyst in the selective adsorption reactions, e.g. in the nanoelectronics applications. As its supplies are concentrated in limited regions of the world, the considerable effort has been made to synthetize it. Besides synthesis from chemical reagents sodium silicate and aluminate, the successful preparations using other economic and locally available sources of aluminosilicate materials, such as rice husk ash and kaolin, natural clinker, coal fly ash, palygorskite, and perlite, were reported [1-5]. More recently, analcime was synthesized via hydrothermal treatment of quartz syenite powder and NaOH solution [6]. In this work we present simple zeolite preparation, which consists of geopolymer transformation under hydrothermal treatment. Homogenized mixtures made from metakaolin and sodium water glass were exposed to 0.5 MPa and 165 °C for different times (6, 24 and 48 hours). The effect of hydrothermal treatment on pore structure and composition of prepared zeolites was studied by means of DTG, XRD, gas sorption analysis, and SEM. In the case of shorter autoclaving and access of water vapour, the mix of different zeolite phases was formed: analcime, zeolite P, zeolite phi, gmelite-Na. From the time of 24 hours, pure cubic analcime was detected. Uniform microstructure of these samples comprised of spherical particles with the diameter between 50–60 μm.

Acknowledgments

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Thermal study of organic-inorganic layered perovskite-like Bi-containing titanate

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Keywords: perovskites, organic-inorganic hybrids, thermolysis, simultaneous thermal analysis

Hybrid organic-inorganic compounds based on layered perovskite-like oxides is a new promising class of materials which properties could be tailored by targeted modification of both organic and inorganic parts. Preparation of such materials are recently focused on a stepwise approaches including subsequent hydrothermal and microwave-assisted hydrothermal intercalation and grafting reactions that lead to the formation of bulk hybrid compounds followed by their exfoliation into 2D organically modified nanosheets. [1] Such hybrid compounds and nanosheets are considered as perspective materials exhibiting photocatalytic, catalytic, ferroelectric, and luminescent properties. Although, the thermal behaviour of such hybrids have not been yet widely studied, their application might be strongly dependent on their thermal stability. Additionally, in some cases, the thermolysis of thermally stable organic-inorganic compounds may lead to the modification of organic part without its complete elimination resulting in the formation of carbon layer in the interlayer space of inorganic host. Such approach, for example, may be used for the synthesis of carbon-modified visible-light photocatalysts.[2]

In the present work we report the results on the study of thermal stability of organic-inorganic materials based on the protonated form of layered perovskite like oxide $H_2K_{0.5}Bi_{2.5}Ti_4O_{13}\cdot H_2O$ belonging to Ruddlesden-Popper phases. N-amines namely, methylamine, n-butyl and n-octylamine has been used as organic modifiers. Amine-intercalated compounds have been obtained by facile room temperature and hydrothermal-assisted reactions between amines and inorganic hosts. The phase purity of all of the obtained samples was controlled by XRD analysis and their composition was characterized by simultaneous thermal analysis (TG + DSC) coupled with mass-spectrometry (MS), FTIR spectroscopy and CHN analysis. The advantages of STA analysis coupled with MS for quantitative analysis of organic hybrids are considered in comparison with CHN analysis. The influence of length of carbon chain in amines on the conditions required for the formation of hybrids and their thermal stability has been studied. It was found that n-butylamine intercalated compound could be easily obtained by facile treatment of the host protonated form by n-butylamine at room temperature for a relatively short time (24h), while the formation of methylamine hybrid requires longer reaction times (up to two weeks) or hydrothermal heating. In case of n-octylamine the preliminarily n-butylamine intercalated HKBT is required as a precursor. Although, n-butylamine hybrid could be easily obtained at room temperature, it demonstrated a higher thermal stability comparing to methylamine-intercalated compound. In this regard, it has been used for a further preparation of carbon/nitrogen-containing composites via thermolysis. Thermolysis was carried out by calcination of the organic-inorganic hybrid at different temperatures, chosen in accordance with results of TG. The structural and composition changes during thermolysis were studied by XRD and CHN analysis. It was found that the complete decomposition of the sample occurs at temperatures above 800ºC, leading the formation of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ after calcination at 1000ºC, and the layered structure is maintained at temperatures below 700ºC. CHN analysis showed a gradual decrease of the hydrogen content in the sample with its complete removal at 350ºC, suggesting the formation of carbon/nitrogen-containing layer.

Acknowledgments

Scientific research was performed at the Research Park of St. Petersburg State University: Thermogravimetric and Calorimetric Research Centre, Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre. This work was supported by RFBR (grant 18-03-00915).

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Kinetics and catalysis

Thermal behavior and kinetic analysis of intercalated phases of α-titanium phosphate

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Keywords: titanium phosphate, intercalation, thermal decomposition, kinetics

In a previous work, our research group described the synthesis of the metallic phases of α-phosphate of titanium including both divalent ions (Co^{2+} and Ni^{2+}) and trivalent ions (Fe^{3+} and Cr^{3+}). It is well known the precursor α-$Ti(HPO_4)_2 \cdot H_2O$ (layered solid that crystallizes in the monoclinic system space group $P2_1/c$) possesses ion- exchange properties with monovalent elements in aqueous media, but it has a low affinity towards divalent and trivalent transition-metal ions [1,2]. In this case, compounds of general formula $TiM^{II}_xH_{2-2x}(PO_4)_2 \cdot yRNH_2 \cdot nH_2O$ (x = 0.0-1.0, y = 0.1-0.8) and $TiM^{III}_xH_{2-3x}(PO4)_2 \cdot yRNH_2 \cdot nH_2O$ (x = 0.00-0.67, y = 0.1-1.1) were prepared through an intermediate phosphate, $Ti(PO_4)_2 \cdot 2C_3H_7NH_3 \cdot H_2O$, obtained by reaction of the precursor with *n*-propylamine. In this way, the interlayer distance increased from 7.6 Å for the initial solid up to 16.9 Å for the intercalated phosphate [3]. Thermogravimetric analysis and X-ray diffraction data led that the thermal decomposition takes place in three sequential stages that were associated with dehydration at moderate temperatures (T < 473 K), amine desorption (573-873 K), and condensation (T > 1173 K).

In this work, we present a deeper study of these compounds. On the one hand, data of TG/DTG/DTA and the associated mass spectrometric signals of the evacuated species are analysed. On the other, kinetic analysis is performed by using isoconversional methods, which allow us to calculate the activation energy as a function of the extent of conversion without knowing the pre-exponential factor or the model function. Differential and non-linear procedures are used and the values of the kinetic parameters obtained are checked by reconstructing the conversion curves and comparing with the experimental data.

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Non-isothermal decomposition kinetics of hydrated volcanic glass (pitchstone)

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Keywords: volcanic glass, dehydration kinetics, isoconversional, Arrhenius equation, pitchstone, perlite

Pitchstone constitutes secondary hydrated amorphous volcanic glass; its water content ranges between 5 and 10% and is chemically bound to its index forming molecular water and OH groups. Sophisticated thermal treatment of hydrated volcanic glass (expansion) allows the production of frothy material that is used in many applications, due to its low density and significant thermal insulating properties. Due to considerable water content of pitchstone, expansion process cannot be applied to raw pitchstone, and a preliminary selective dehydration step is needed to selectively remove the excessive water content and maximize the material expansion performance.

Dehydration kinetics of fine pitchstone samples have been studied through thermogravimetric analysis in air atmosphere under 4 different heating rates (2, 5, 10, 20 °C) and heating temperature between 25 and 800 °C. Dehydration extends to temperature between 200 and 600 °C, and weight loss rates maximize between 257 and 306 °C. Under these conditions pitchstone samples weight loss range between 7.04 and 7.40 % wt. and is solely attributed to water species release. Apparent activation energy (E_a) of pitchstone dehydration has been calculated through rate and integral isoconversional methods. The calculated E_a values of both methods are similar throughout the conversion degree, exhibiting mean value of 109.8 kJ/mol at conversion between 0 and 0.7. Determination of pre-exponential factor and reaction model was performed through masterplots method, and it was found that pitchstone dehydration obeys the F_n model, with n value between 5 and 6. The model predictions are in agreement with the experimental data.

Effect of interparticle diffusion on methane catalytic oxidation performance on reverse flow reactors

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Keywords: Reverse flow reactor, Intraparticle diffusion, effectiveness factors dynamic.

The catalytic reaction is a heterogeneous process typically involves gas and solid phases. To analyze its performance, the effects of interparticle diffusion must be considered in order to figure out the effects of alternating flow on a Reverse Flow Reactor (RFR) on the reaction rate. RFR is a fixed bed reactor where the flow direction periodically changes at any given time. In these flows, the tortuosity value behaves dynamically. It affects interparticle diffusion and eventually impacts the reaction rate.

To evaluate the influences of interparticle diffusion on reaction rate is approached by determining effectiveness factors. In this work the effectiveness factors of the reaction was estimated by modeling and simulation using FlexPDE finite element model builder for Partial Differential Equations. The procedure is carried out by taking into account the barriers due to intraparticle diffusion in any point of the reactor without numerical integration of diffusion equations in the pellet.

This approach was done to resolve the spatial steps which arising due to the changes in flow direction. The results obtained from the simulation were verified by the experiment carried out in the RFR module. The simulation results satisfactorily fit for the experimental model. The reverse flow operation in the fixed bed reactor produces the effectiveness factors which changes dynamically. In particular it can improve the performance of reactor compare to the steady-state condition. The developed model has been validated for understanding the dynamic behavior of methane oxidation in RFR.

Kinetic analysis of the thermal decomposition of cerium(iv) phosphates

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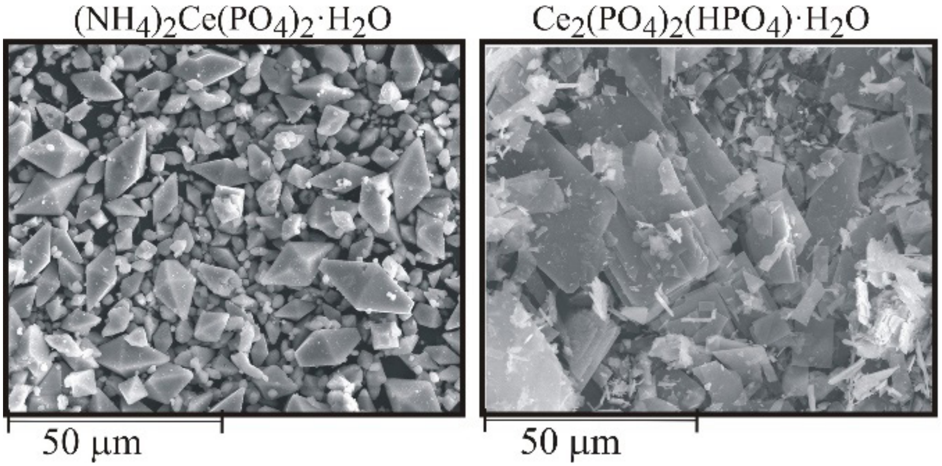
Keywords: cerium phosphate, thermal decomposition, kinetic analysis

Cerium(IV) phosphates (CePs) have been first studied in the late sixties by König *et al.* [1]. Subsequently, Alberti and Clearfield synthesised a large number of these phosphates with different crystal structures [2,3] and P/Ce ratios ranging from 1:1.1 to 3.0:1. Although the most of their crystal structures remain unknown, the properties observed for these solids made them interesting for applications in the area of catalysis, ion-exchange, trapping of radioactive elements and proton conduction [4].

Two cerium(IV) phosphates, $(NH_4)_2Ce(PO_4)_2\cdot H_2O$ [5] and $Ce_2(PO_4)_2HPO_4\cdot H_2O$ [4] have been hydrothermally obtained, in a stainless steel Teflon-lined vessel under autogenous pressure, by using cerium oxide as the source of metal. Microcrystals of the first phosphate were synthesised from the CeO_2-$CO(NH_2)_2$-H_3PO_4-H_2O system (180 ºC, 5 days) and the second was obtained from CeO_2-H_3PO_4-H_2O system (180 ºC, 40 hours). As can be seen on the SEM images, the morphology of these compounds is very different. Kinetic parameters of the thermal degradation of the materials were obtained from thermogravimetric data. The samples were heated from 25 to 1000 °C under a nitrogen atmosphere with different constant heating rates. Isoconversional methods [6] are used to carry out the kinetic analysis.



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Thermal degradation kinetics of newly synthesized arylazo pyridone dyes

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Keywords: Arylazo dyes; Degradation; Thermal stability; Kinetics behaviour; Heterolytic splitting

Thermal degradation properties of the newly synthesized azo dyes derived from 6-hydroxy-4-methyl-2-okso-1,2-dihydropyridine-3-carboxamidewere examined. Depending on the nature of substituent that is located on the para position of the diazo components of azo pyridone dyes, different thermal stability can be obtained.The thermal behaviour of the present dyes has been determined using thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). On the basis of this method, non-isothermal kinetics was monitored. To explain kinetics behavior of the investigated dyes during their degradation in an inert atmosphere, ASTM E698, ASTM E2890, Friedman's (FR), Ozawa-Flynn-Wall (OFW) as well as Kissinger-Akahira-Sunose (KAS) isoconversional (model-free) methods were applied. Numerical optimization was used in order to judge fitting capabilities including simulated and experimental curves, for estimated kinetic parameters. It was found that different thermal stabilities of various dyes are the consequence of their different chemical structures, including diverse substituents. It was shown that significant difference in reactivity for hydroxy substituted and unsubstituted dyes is a consequence of reactivity dissimilarities between •OH and H• species.It was assumed that reactions with ˙OH are characterized with changing in limiting stage, from kinetic to diffusion controlled. The numerical optimization shows a good fitting correlation between experimental and simulated process data. Based on multi-level conversion analysis, using differential (FR) and integral (OFW and KAS) model-free methods, the all dyes, exhibit the different *E*-conversion dependency.

Acknowledgments

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Kinetic extraction of the thermal decomposition steps of pigment molecules from the multistep thermal decompostion of maya blue-type pigments

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Keywords: Maya blue, pigment, thermal decomposition, multistep reaction, kinetic deconvolution analysis

Maya blue is an ancient pigment synthesized by incorporating pigment molecules into micropores of clay mineral substrates. The excellent properties of Maya blue with regard to thermal resistance, light resistance, and water resistance attract researches to reveal the structural and physico-chemical origins [1,2]. Although a detailed kinetic study of the thermal decomposition of Maya blue is required for evaluating the thermal resistance of Maya blue, the overall thermal decomposition is a complex multistep reaction. In this study, extraction of the thermal decomposition steps of pigment molecules from the multistep thermal decomposition of Maya blue was examined through the kinetic deconvolution analysis [3].

The samples were prepared by incorporating pigment molecules (indigo, methyl red, or alizarin) into clay mineral substrates (palygorskite or sepiolite) by stepwise thermal treatments for the mixtures and subsequent purification of as-prepared Maya bule-type pigments [4], obtaining blue pigment (Maya blue, MB), red pigment (Maya red, MR), and yellow pigment (Maya yellow, MY). The thermal decomposition processes of the clay mineral substrates and the Maya blue-type pigments were tracked using TG–DTA (STA7300, Hitachi) at different heating rates β, and subjected to the kinetic analysis.

In Fig. 1 are shown typical results of the kinetic deconvolution analysis of the thermal decomposition of the clay mineral substrate and the Maya blue-type pigment, as exemplified by palygorskite and MB (palygorskite-indigo). The thermal decomposition of palygorskite and sepiolite were characterized kinetically as the overlapping four and five reaction steps, respectively. For the thermal decomposition of MB, MR, and MY, several additional reaction steps were observed in comparison with the thermal decomposition of the clay mineral substrates. Those additional steps were expected to be attributed to (1) sublimation/decomposition of pigment molecules, (2) decomposition of pigment molecules incorporated in micropores of the substrate, and (3) oxidative decomposition of the pigment residue. The kinetic features of the thermal decomposition of pigment molecules in Maya blue-type pigments are discussed in comparison with that of the free pigment molecules.

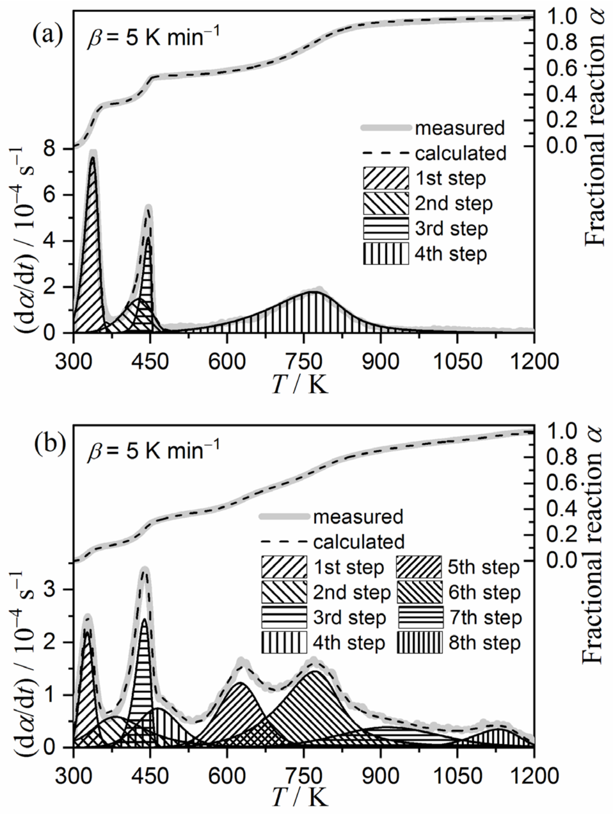

Fig. 1. Typical results of the kinetic deconvolution analysis
for the thermal decomposition of (a) palygorskite and (b) palygorskite-based MB.

Acknowledgments

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Influence of agglomeration of the glass set on the melting of sodium-calcium-silicate glass with increased content of substitute raw materials

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Keywords: glassy waste, Calumite slag, thermal analysis, agglomeration

Currently, more and more attention is paid to the rational use of raw materials. Actions in this area include the elimination of various types of dust and dust materials from the production cycle. The batch of the glassware in the form of a dry and loose mixture always leads to the segregation of ingredients. Due to the different density and particle size of the raw material dusting occurs. The use of a compact glass set in the form of granules is advantageous in view of minimizing the delamination of raw materials and significant reduction of dusting. The thermal conductivity and improvement of the energy efficiency of the melt increases. The influence of sets of 60% of the colorless cullet and 15% Calumite slag treated as a raw material substitution on the process of batch melting was studied. The tested glass sets were compacted by mechanical compression. The research was conducted using, differential thermal analysis (DTA) and thermogravimetry (TG) based on a composition of model glass [wt.%]: 73.0% SiO_2, 1.0% Al_2O_3, 10.0% CaO, 2.0% MgO and 14.0% Na_2O. The influence of sulfate and multicomponent fining agent – a mixture of As_2O_3, Sb_2O_3, $NaNO_3$ in the proportions of 1: 1: 1 on the chemical reaction and phase transformation were tested. It was found that compaction of a loose glass set by pressing resulted in raising the temperature of all reactions related to the decomposition of carbonates. There is a decrease in the degree of decomposition, expressed by the amount of weight loss accompanying the given reaction stage in the glass set. This is due to the impeded release of CO_2 as a reaction product, when the set is compacted, its pressure (partial pressure in the pores) increases in the glass set.

Thermo-gravimetric analysis of bagasse fractions (Fibre and pith) for solid fuel beneficiation in boilers, stoves, and open fires

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Keywords: Fibre, pith, activation energy, reaction rate, volatilisation, carbonisation

Effective separation of bagasse fractions of fibre and pith to be beneficiated as solid fuels opens up new opportunities opens up energy potential for use in boilers, stoves and open fire applications. Their potential use as briquettes would require the characterization of their thermal behavior and degradation which is vital for the determination of the best fraction with better thermal behavior. Thermo-gravimetric analysis of bagasse, fibre and pith fractions were carried out under inert atmospheres. Thermal degradation of fibre and pith briquettes took place in two stages of volatilization and carbonization. Kinetics factors: reaction rate, activation energy, entropy change, enthalpy change and Gibbs free energy were calculated. Results indicate that fibre briquettes have high activation energy and reaction rate for volatilization which indicated least of activation energy and reaction rate for carbonization while pith fraction indicates a contrary behavior. The implication is that potential fraction of bagasse can be deployed used as the solid fuels in the form of bagasse for boilers, stove and open fires.

Computational approaches for modeling biomass pyrolysis: slow pyrolysis process of apricot kernel shells controled by non-isothermal simultaneous thermal analysis (STA)

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Keywords: Pyrolysis; Modeling; Apricot wastes; Kinetics; Fraser-Suzuki; Kinetic model function

Pyrolysis of lignocellulosic biomass is a promising process capable of producing renewable fuels and chemicals that are currently derived from non-renewable sources. However, industrial pyrolysis processes to make these products from biomass are not yet economically viable and require significant optimization before they can contribute to existing oil-based transportation and chemical systems. One means of optimization uses kinetic and transport models for predicting the products of biomass pyrolysis, which serve as the basis for designing pyrolysis reactors capable of producing the highest value products. In this work, two computational approaches applied in modeling the complex pyrolysis process of biomass were presented. First approach encompasses iterative isoconversional method established in generic codes in MATLAB program. Second approach represents the use of Fraser-Suzuki fitting function for resolving the rate curves that arise from complex process of lignocellulosic materials. In the latter case, every identified reaction step was considered through mechanistic description, which involves selection the appropriate kinetic model function. Comparison of the results as well as discrepancies between them has been discussed. As an example, the slow pyrolysis of apricot (Prunus armeniaca) kernel shells was taken into the consideration, where devolatilization process is monitored using the simultaneous thermal analysis (STA).

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Thermal transformations of Molybdenum (VI) and Vanadium (V) OXO-Species on the surface of γ-Alumina supported molybdena- and vanadia-based catalysts

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Keywords: MoO3/γ-Al2O3- and V2O5/γ-Al2O3-based catalysts, Al2(MoO4)3, AlVO4, phase composition, thermal stability

γ-Alumina-supported molybdenum oxide-based systems are widely used as the catalysts for many industrially important reactions. However, at T > 700°C, MoO3, supported on alumina, exhibits its mineralizing properties causing the intensive sintering and phase transitions in Al2O3 (γ-Al2O3 → δ-Al2O3 → θ-Al2O3→ α-Al2O3) [1, 2]. Some authors [1] suppose that an acceleration of these processes is explained by a relatively low melting point of MoO3 (~795°C). But other investigators [2] associate the intensification of sintering and phase transitions in alumina support with the formation and subsequent decomposition of Al2(MoO4)3. Similar transformations (but with formation of AlVO4) occur in the course of thermal treatment of V2O5/γ-Al2O3 systems [3, 4].

In the present work, the thermal behavior and processes of phase and structure formation in (0–25 wt.%) MoO3/γ-Al2O3 and (0–25 wt.%)V2O5/γ-Al2O3 catalysts during their thermal treatment in air have been studied using thermal and X-Ray diffraction analyses. Catalysts were prepared by impregnating commercial γ-Al2O3 (A-64, S = 200 m2/g) with aqueous solutions of corresponding salts [(NH4)2Mo2O7, NH4VO3, (NH4)2Cr2O7 and Ni(NO3)2·6H2O] followed by drying (12°CC, 4 h) and calcination (600°C, 6 h) of impregnates in air after each component deposition. The samples prepared were subjected to thermal treatment in both temperature-programmed (20–1000°C, 10°C/min) and fixed-temperature (600, 800 and 1000°C, 6 h) regimes of heating.

It has been shown that in the presence of MoO3 and V2O5 the phase transitions in Al2O3 (γ → δ,θ), normally observed at T > 900°C, occur at already 700-900°C. It has been concluded that exotherms at 700–900°C in thermograms of molybdena-alumina and vanadia-alumina samples, accompanying these phase transitions, were not associated with structural transformations of Al2O3 but rather with the processes of bulk aluminum molybdate and aluminium vanadate formations from surface Mo (VI) and V (V) oxo-species, respectively; the posterior decomposition of Al2(MoO4)3 and AlVO4 (at T > 900–950°C) facilitates the formation of θ- and/or α-Al2O3. Cr2O3 added to 13 wt.% MoO3/γ-Al2O3 catalyst has been shown to suppress mineralizing action of MoO3 on the phase composition of Al2O3 [as a result of generating more refractory Cr2(MoO4)3 and/or CrxAl2-x(MoO4)3 phases], and it stabilizes the spinel lattice structure of alumina support (due to the formation of Cr2O3-Al2O3 solid solutions on the base of aluminum oxide). Analogously, introduction of NiO into 10 wt.% V2O5/γ-Al2O3 catalyst retarded phase transitions in Al2O3 at the expense of formation of surface nickel (II) aluminate and V2O5 binding to form thermally more stable nickel vanadates.

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Kinetics parameters determination in non-isothermal conditions for the decomposition reaction of calcium carbonate by modified kinetic equation

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Keywords: The validity function; Thermal decomposition; Calcium carbonate; Model-fitting method; Non-isothermal conditions

The modified kinetic equation, which included the validity function, has been applied to analysis the data for non-isothermal thermal decomposition of calcium carbonate. The true activation energy has been obtained by the trend extrapolation under the differential condition. The re-exponential factor and the reaction model can be uniquely determined by comparing the result of the model-fitting method with the true activation energy. It is shown that, the modified kinetic equation is meaningfully applicable to determine the kinetics parameters for the decomposition reaction of calcium carbonate under non-isothermal conditions.

Using Potassium Permanganate to enhance Titanium Dioxide Photo-catalysis of Methyl Orange

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Keywords: Titanium Dioxide, Methyl Orange, Potassium Permanganate, Hydroxyl Radicals

Many toxic, persistent and non-biodegradable dyes require special studies with the advanced oxidation processes (AOPs) applications, especially Titanium Dioxide (TD). As some oxidants adding into the system, previous studies indicated that the band-gaps could be reduced and the photo-catalytic efficiency could be enhanced owing to the increased production of hydroxyl radicals as well as the hindering of recombination of electronic hole pair. This study used a photo-catalysis reactor with the Taguchi method for photo-catalysis of Methyl Orange (MO) on the factors of light wave length, oxidants and dissolved oxygen as well as the production of hydroxyl radicals (·OH). Using potassium permanganate with TD under ultraviolet light, MO removal could reach above 95% with normal dissolved oxygen in solution. The production of •OH could increase 8 folds but less than that degrading AO7. Different degradation pathways might consume different amount of•OH and, hence, reduce the detection of •OH.

Thermal behaviour of aluminum-iron-vanadium phosphates precursors of beige ceramic pigments

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Keywords: aluminium, iron, vanadium, phosphates, thermal decomposition, kinetics

Modifications of physical properties of solid solutions can be associated with dopant cations and changes in the structure of compounds. Phosphates have a great capacity to form solid solutions and to accept substitutes. The solid solution formation, $Al_{1-x}Fe_xPO_4$, between $FePO_4$ and $AlPO_4$ takes place by the incorporation of Fe^{3+} ions into the $AlPO_4$ structure for $x < 0.5$, while for $x > 0.5$, Al^{3+} ions are incorporated into $FePO_4$. The calcined samples exhibit a semiconductor trend and at temperatures ≥ 600 °C exhibit a ferromagnetic behaviour at rich $FePO_4$ content. It is due to the decomposition of $FePO_4$ to different phases such as Fe_3PO_7 and α-Fe_2O_3 [1].

Some structures of phosphates can be used as ceramic pigments in addition to oxides and silicates [2]. The d-d

electronic transitions within transition metal ions give rise to many colours. The strong absorbance due to charge transfers is the most important component in the coloration of some solid solutions. The incorporation of small amounts of V(V) ions by substitution of P(V) ions in a structure changes the bond strength and modifies the colour of the materials. Changes in colour can also be obtained by changes in M-O distances and coordination numbers when M is incorporated in different structures [3].

Recently, $Al_xV_yFe_{1-x}P_{1-y}O_4$ ($0.0 \le x \le 0.3$, $0.0 \le y \le 0.1$) compositions were synthesized via the chemical co-precipitation method, and optimal beige materials to work without sample fusion at 1200 °C are obtained from the composition with $x = 0.2$ and $y = 0.05$ ($Al_{0.2}V_{0.05}Fe_{0.8}P_{0.95}O_4$) [4]. The starting materials were $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, H_3PO_4 and NH_4VO_3. The stoichiometric amount of NH_4VO_3, a 0.5 M solution of H_3PO_4 in water, $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were added to water to obtain a final volume of 200 mL. Samples were vigorously stirred for two days at room temperature. Subsequently, an ammonia aqueous solution was added until reaching pH = 10 and precipitation of materials was obtained. All samples were characterized, among others, by powder X-ray diffraction (PXRD), scanning and transmission electron microscopies (SEM, TEM), thermogravimetric analysis (TG-MS-DTG-DSC).

In the present work, applying isoconversional methods, we will show the kinetic parameters of the thermal decomposition of the raw materials, previously dried by IR-irradiation.

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The influence of vitreous waste entropy on sintering process

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Keywords: glassy waste, fly ash, sintering process, entropy, devitryfication.

There is a fairly large range of waste that is partially or fully vitrified eg: fly ashes, granulated slag, cullet. As long as they are not loose, after milling these wastes are an interesting raw material for the production of sintered ceramics. In this application, attention is usually paid to their fluxing effect during sintering, due to the high content of alkali oxides and iron oxide.

The high entropy of these raw materials resulting from the large proportion of glassy phase is usually neglected. In this paper, we shown that during the sintering of glassy wastes their entropy decreases, which is mainly the result of their devitrification and previous glass transformation. Both the sintering process and the processes associated with the drop in glass entropy are exothermic. Their simultaneous coexistence causes that they can accelerate each other. The influence of high entropy of vitreous wastes on the acceleration of the sintering process was demonstrated with use of thermal studies such as DTA/TG, dilatometry and high temperature microscopy. The fly ash, ground cullet and their mixture were used as glassy wastes.

Synthesis of V_2O_3@C composite materials as Pt-free counter electrodes for dye sensitized solar cells by single step reduction with soluble starch

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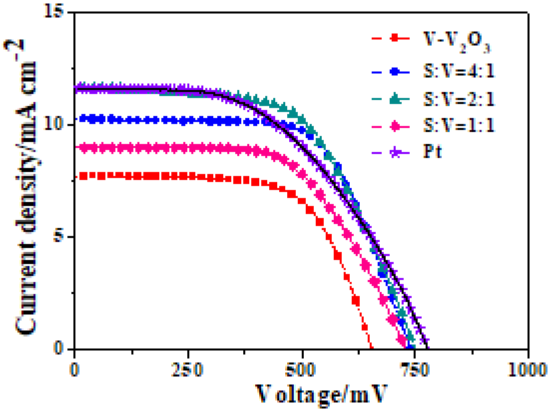
Keywords: dye-sensitized solar cell, counter electrode, Vanadium (III) oxide, composite material, power conversion efficiency

V_2O_3@C composite catalysts with different mass ratios have successfully been prepared using a facile one-step the reduction of V_2O_5 with soluble starch in a high-temperature solid-state reaction. V_2O_3@C composites were further served as catalytic materials for counter electrodes (CEs) in encapsulation of dye sensitized solar cells (DSSCs). The morphology and microstructure of each V_2O_3@C composite were determined by scanning electron microscopy and X-ray diffraction. Cyclic voltammetry studies revealed that the V_2O_3@C composites showed a higher electrocatalytic activity than V_2O_3 for the reduction of triiodide ions. Electrochemical impedance spectroscopy and Tafel analysis data for the symmetrical cells indicated a lower charge transfer resistance and higher exchange current density for V_2O_3@C composite than V_2O_3. The experimental results showed that power conversion efficiencies(PCE) of 3.94, 5.13 and 4.97% were obtained for soluble starch: V_2O_5 mass ratios of 1:1, 2:1 and 4:1 as counter electrode toward the reduction of I_3^-/I^- ions respectively, which were superior to higher than that of V_2O_3(3.33%) electrode under the same conditions. The enhanced electrode performance can be ascribed to the combined effects of the relatively larger surface area and higher conductivity of V_2O_3@C composite catalysts.



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Influence of the adjacent layers on the crystallization kinetics of $Ge_2Sb_2Te_5$ thin films

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Keywords: phase-change memory, Ge2Sb2Te5, crystallization

Materials of the Ge-Sb-Te system have found application in non-volatile phase-change memory devices. In particular, the Ge2Sb2Te5 compound is considered the most promising. The recording rate of these devices is limited by the crystallization as the slowest process. However, despite the fact that this type of memory is already implemented in portable devices, the characteristic features and mechanism of the crystallization are not well understood. Crystallization kinetics is actively investigated using thermal methods for studying materials, for example, by the method of differential scanning calorimetry (DSC). However, in this case, a thin film is scraped from the substrate and pressed in the crucibles. Therefore, these results may differ from those for the real thin-film structures. Since the phase-change memory cell is a multilayer structure, layers contacting with the GST225 thin film can influence the crystallization kinetics. Therefore, the purpose of this work was to study the effect of sublayers on the crystallization kinetics of Ge2Sb2Te5 thin films using investigation of the resistivity temperature dependences in comparison with the DSC measurements.

GST225 thin films were deposited by magnetron sputtering. The composition of the films was studied by Auger spectroscopy (Perkin Elmer PHI-660) and is close to the original GST225. The thicknesses of the films were determined by atomic force microscopy (NT-MDT Solver Pro) and were close to130 nm.

Thermal properties and thermally induced transformations were studied using differential scanning calorimetry (DSC-50, Shimadzu). Scraped films from the substrates were used and pressed in Al pans. For these samples, exothermic peaks were observed with the maximums in the temperature range 165÷180 °C, which corresponds to the phase transition from amorphous state to a metastable cubic structure of the NaCl type.

The resistivity temperature dependences were studied by a special set-up, containing the heating stage HFS600E-PB4 Linkam and picoammeter Keithley 6485. In this case, the samples had planar structures consisting of an oxidized silicon substrate with formed TiN/W/TiN electrodes between which different layers of conducting materials (Ti, Al, TiN, W, TiN+W, Ni) were deposited. For studying the crystallization kinetics by both methods, measurements were performed at different heating rates (from 5 to 30 °C/min).

For the investigation of crystallization kinetics, a technique earlier developed for the results of DSC studies [1] was adopted for the results of studying resistivity temperature dependencies of thin films. The essence of this technique is the joint use of the model-free of Ozawa-Flynn-Wall and the Coates-Redfern model-fitting methods.

Measurements of the resistivity temperature dependences showed that in the range from room temperature to 165 °C there is exponential temperature dependence characteristic for the amorphous state. In the range of 165–185 °C, there is a sharp drop in resistivity by almost two orders of magnitude, which is due to the phase transition from the amorphous to crystalline state.

As a result, for DSC method it was found that the effective activation energy at the beginning of the process was 1.8 eV, and reached 1.7 eV at the end of the process. This result differs significantly from those obtained for thin film structures. It was established that the values of the effective activation energy obtained from the results of the measurements of the resistivity temperature dependences are higher than those obtained by DSC. For example, it was found that Ti sublayer increases the value of the effective activation energy at the beginning of the phase transition process, as compared with the oxidized silicon substrate (from 3.3 to 3.5 eV). However, by the end of the phase transition from the amorphous to crystalline state, the activation energy values are nearly equal. Influence of the other adjacent sublayers on the effective activation energy was analysed.

Thus, it was revealed that the different layers of conducting materials influence the crystallization kinetics of GST225 thin films.

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Mechanisms and kinetics of the thermal decontamination of tritium and radiocarbon in spent activated carbon

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Keywords: spent activated carbon, thermal desorption, radiocarbon, partial oxidation, kinetic analysis

The nuclear industry generates spent GACs (granular-type activated carbons) to be disposed of in a radioactive waste repository. Owing to the high disposal cost and the shortage of available land, developing a thermal decontamination process to convert radioactive spent GACs into free-releasable waste is an attractive goal from an economic perspective. The major radioactive contaminants in GACs are tritium (^{3}H) and radiocarbon (^{14}C), which are adsorbed mostly in the form of H_2O and CO_2, respectively. This study investigated the mechanisms and kinetics of the thermal decontamination of ^{3}H and ^{14}C species in spent GACs.

The results of a non-isothermal TG analysis with a FTIR gas analysis showed three weight loss steps. The first weight-loss step started at 60 °C. The first and the second reaction steps overlapped at temperatures between 170 °C and 220 °C. The second weight-loss step finished at approximately 530 °C. Most adsorbed H_2O and CO_2 species were removed during the first and the second weight-loss steps. A further weight-loss step, the third, during only CO_2 species were emitted, started at 530 °C and continued to 1200 °C, showing a very slow and nearly linear weight loss rate with the temperature. This indicated that the third weight-loss step occurred due to the outgassing of adsorbed species existing in the microspores of GACs and that its rate was therefore much slower and did not significantly increase with the temperature.

Vacuum thermal desorption processing at 1200 °C and approximately 10^{-7} bar could reduce the outgassing time of adsorbed species in the microspores. However, the level of ^{14}C in GACs after this vacuum thermal desorption process still slightly exceeded the free release criterion of ^{14}C. This suggests that a small fraction of ^{14}C existed in the form of thermally stable carbon elements in the graphite structure of GACs. There may be an exchange reaction between ^{14}C in the adsorbed gaseous species, such as $^{14}CO_2$ and $^{14}CH_4$, and a stable carbon element in the graphite structure of spent GACs during the course of heating to 1200 °C.

Partial oxidation tests for the peeling of vacuum treated GACs were conducted to assess the potential to remove thermally stable ^{14}C species in the graphite structure of GACs. The peeling process was found to be effective for reducing the level of ^{14}C to a level below the established free-release criterion. A non-isothermal kinetic analysis and a prediction of the oxidative peeling process were also conducted to establish the optimum process condition without the need to use unnecessary energy or time.

Life sciences

Telling signs of plasma DSC thermograms on patients with psoriasis

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Keywords: psoriasis, blood plasma, DSC, thermogram, deconvolution

Psoriasis is an inflammatory disease that changes plasma composition and it is detectable by Differential Scanning Calorimetry (DSC). Besides the general change of plasma, the aim of the study was to demonstrate which components are changing and how the anti-psoriatic drug treatment affects back to all this. Retrospectively, blood plasma DSC data were analyzed from patients, who has different severity of symptoms (n=10) and who received (n=5) or not (n=6) drug treatment. Complex thermograms were deconvoluted in several individual transitions (peaks), modelling each individual transition. In the examined psoriasis stages the thermodynamic parameters: excess heat capacity and enthalpy of the transitions corresponding to the most abundant plasma proteins, as well as the numbers of transitions were determined from the calorimetric profiles. Deconvoluted plasma DSC profiles showed similarities but exhibited marked differences in the thermal denaturation on different treated and non-treated psoriasis stages.

Effects of different temperature regimes on survival of Diaphorina citri and its endosymbiotic bacterial communities

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Keywords: microbial ecology, endosymbionts, wolbachia, thermal stress

The Asian citrus psyllid, *Diaphorina citri*, is a major pest of citrus and vector of citrus greening (huanglongbing) in Asian. The aim of this investigation was to examine the effects of temperature regimes on survival of *D. citri* and its primary and secondary endosymbiotic bacterial communities. The effects of exposure duration and the host insect gender on the endosymbionts under different temperatures were also explored. In our field-collected psyllid samples, we discovered that Fuzhou (China) and Faisalabad (Pakistan), populations harbored an obligate primary endosymbiont Candidatus Carsonella (gen. nov.) with a single species, *Candidatus* Carsonella ruddii (sp. nov.) and a secondary endosymbiont, Wolbachia surface proteins (WSP) which are intracellular endosymbionts residing in the bacteriomes. Responses of these symbionts to different temperatures were examined and their host survival assessed. Diagnostic PCR assays showed that the endosymbionts infection rates were not significantly reduced in both *D. citri* populations after 24 h exposure to cold or heat treatments. Although quantitative PCR assays showed significant reduction of WSP relative densities at 408C for 24 h, a substantial decrease occurred as the exposure duration increased beyond 3 days. Under the same temperature regimes, *Ca.* C. ruddii density was initially less affected during the first exposure day, but rapidly reduced at 3–5 days compared to WSP. However, the mortality of the psyllids increased rapidly as exposure time to heat treatment increased. endosymbionts. The responses of the two symbionts to unfavorable temperature regimes highlight the complex host-symbionts interactions between *D. citri* and its associated.

Comparative study of the thermal behaviour of Sr-Cu-O gels obtained by sol-gel and microwave assisted sol-gel methods.

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Keywords: strontium cooper oxide, sol-gel method, microwave assisted sol-gel method, nanopowders, thermal properties

In the literature data several papers reported the synthesis by various chemical or physical methods of the $SrCu_2O_2$ (SCO) having possible applications as: thermoelectric or full oxide electronic devices or films as: solar cells, liquid crystal displays, touch screen, so on. A great challenge is the formation of the pure $SrCu_2O_2$ (SCO) due to the high labiality of the Cu valence, depending on temperature. In the present work the thermal behaviour of Sr –Cu-O gels obtained by sol–gel or microwave assisted sol-gel methods was studied in order to establish the thermal conditions for pure nanostructured $SrCu_2O_2$ preparation. As reagents strontium and copper acetate and acetylacetonate in acetic and alcoholic media were used. The starting solutions were homogenized either by stirring for 2 hours at room temperature or were exposed to microwaves (MW) for 5 min at 300 W and a frequency of 2.45 GHz and left to gel at room temperature. Both obtained gels were investigated by TG/DTA-MS measurements in air, inert and reducing atmospheres. A stepwise thermal decomposition of the gels was noticed in a large temperature range, up to 900^{o}C. The powders thermally treated at 900°C have been characterized by Fourier-Transform Infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The results put in evidence the influence of the MW on the sol-gel synthesis and on the thermal properties of the resulted gels. Based on the obtained results the required thermal treatment of the gels in order to obtain nanostructured powders with the $SrCu_2O_2$ composition was proposed.

Acknowledgments

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Effects of temperature on lifespan of Drosophila melanogaster from different genetic backgrounds: links between metabolic rate and longevity

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Keywords: aging, development, fruit fly, isothermal calorimetry, lifespan

Despite many studies of the aging process, clear answers to the questions on key factors that ensures longevity have not yet been found. It seems that temperature is one of the most important factors regulating lifespan. However, the genetic background may also play a key role in determining lifespan [1]. Therefore, the aim of this study is to investigate the relationship between temperature, genetic background (fruit fly origin) and the rate of metabolic parameters measured as energy flow. Experiments were performed with wild type lines of *Drosophila melanogaster* originating from Australia [2,3], Canada [4] and Benin [5], and the OregonR strain (Bloomington Drosophila Stock Center). Flies were maintained in the laboratory, on standard fly medium, at 20°C, 25°C and 28°C, a light/dark cycle of 12/12 h, RH 60%. Metabolic activity of *D. melanogaster*, understood as heat rate values (*Rq*), was measured at 20ºC, 25ºC and 28ºC in a TAM III isothermal calorimeter (TA Instruments). Five specimens of each strain, male and female separately, were placed in 4.0 mL calorimetric ampoules with 0.5 mL of agar with apple juice. The calorimeter recorded the heat rate in μW ($\phi = dQ/dt$) continuously over 24 hours The quantitative heat rate (metabolic activity) was determined by integrating the ϕ-t plots over a time interval of 24 hours to give the heat rate (*Rq*) in mJ per body weight of the flies and hour (mJ mg^{-1} h^{-1}). The impact of the origin of flies on heat rate in individual temperatures was determined (separately for males and females) using the two-way ANOVA.

Our data show that temperature affects the lifespan of the four lines differently. We find a strong negative relationship between heat rate and longevity. A high metabolic rate leads to increased aging in males and females in all strains while low metabolic levels reduce the heat rate and increase longevity. This suggests that metabolic rate is crucial in determining longevity. Our results further show that temperature has a significantly effect on fertility, reproductive success and body weight of males and females in *D. melanogaster*.

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Evaluation of collagen in saphenous vein on the basis of kinetic parameters of its thermal denaturation

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Keywords: collagen, DSC, isoconversional method, Kissinger method, varicose vein

Chronic venous insufficiency is one of civilization diseases affecting adults. The main symptom are varicose veins at lower limbs resulting from weakening of the vein wall and venous valves. Physical properties of the veins depend directly on the collagen content and arrangement within the vein wall. Collagen, a fundamental protein of the connective tissue, cooperates with other components of the vein wall, in order to ensure a proper level of the wall stiffness and elasticity.

The objective of the study was to compare collagen in efficient and inefficient parts of the saphenous veins with chronic venous insufficiency. Collagen in veins samples was characterized in terms of parameters of thermal denaturation obtained from differential scanning calorimetry (Q200, TA) for temperatures from 15°C to 90°C. Kinetic analysis of denaturation was performed on the basis of DSC measurements at different heating rates (0.5K/min – 10K/min). As a reference the same measurements and analyses were performed for purchased collagen type I.

The thermograms were analysed both in the terms of a single first-order irreversible process [1] and as a two-step process: a reversible transition between native and unfolded states followed by an irreversible transition between unfolded and denatured molecules [2-4]. Thermograms obtained at increasing scanning rates showed a shift towards higher temperatures. Moreover, the further analysis revealed the dependence of activation energy on the denaturation degree. These findings are consistent with the two-step model, however for low heating rates the differences between these two approaches were negligible.

The differences in the thermal denaturation of collagen in different layers of the vein wall were found both as temperature shift and as different activation energies. However, differences between sufficient and insufficient parts of the vein were expressed more in the terms of energy than in temperature.

Results suggest a nonhomogeneous population of collagens in different layers of vein wall. These differences may be related to the different collagen types, the content of covalent cross-links, and the content of elastin and glycosaminoglycans. Differences between sufficient and insufficient veins can be useful for discussing a nature of collagen alterations in varicose veins.

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Materials science

Martensite stabilization effect and the transformation enthalpy in the deformed NiTi shape memory alloys

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Keywords: DSC, martensitic transformation, thermodynamics, martensite stabilization effect, NiTi shape memory alloy

Martensite stabilization effect in NiTi shape memory alloys is reveals as an increase in the temperatures of the reverse martensitic transformation during the first heating of the preliminary deformed samples. The larger the preliminary strain, the higher the temperatures of the reverse transformation. Besides the shift in the transformation temperatures, a decrease in the reverse transformation enthalpy is found. The aim of the present paper is to study the nature of the variation in the transformation enthalpy during the martensite stabilization effect in NiTi shape memory alloys. Two NiTi alloy plates with the Ni concentration of 50.0 at. % ($Ni_{50}Ti_{50}$) and 50.5 at. % ($Ni_{49.5}Ti_{50.5}$) were quenched from 900 ^{o}C into water to prevent the precipitates formation. After such heat treatment the alloys underwent the B2 ↔ B19' martensitic transformation on cooling and heating at different temperatures depending on the alloy composition. Both alloys were subjected to preliminary deformations by two ways: active deformation up to different strain varied from 1 to 25 % in the martensite state (at room temperature) or cooling under a constant stress through the temperature range on the forward B2 → B19' transformation. The samples with a size of 3x3 mm were cut from the central part of the deformed samples by electro-discharge machine and used for calorimetry study. In differential scanning calorimetry "Mettler Toledo" 822e the samples were heated to 200 ^{o}C, cooled to -20 ^{o}C and heated to 200 ^{o}C to study the martensite stabilization effect. As expected, the temperatures of the reverse transformation during the first heating were higher than during the second heating. It was found that an increase in the preliminary strain decreased the reverse transformation enthalpy measured during the first heating as well as during the second heating. Moreover, the enthalpy of the forward transformation that occurred on cooling after the first heating decreased in the same way. As a decrease in the reverse transformation enthalpy was observed both during the first and the second heating, hence it was not caused by the martensite stabilization effect because it was revealed during the first heating only. The comparison of the data found in two different alloys showed that in the $Ni_{50}Ti_{50}$ alloy a decrease in the transformation enthalpy on an increase in the preliminary strain began immediately i.e. it was observed even after a small preliminary deformation. In the $Ni_{49.5}Ti_{50.5}$ alloy an increase in the preliminary strain to 7% did not affect the transformation enthalpy, whereas, further increase in the preliminary strain to 15% decreased the enthalpy from 23 J/g to 15 J/g. As these two alloys are differed by the ability for the plastic strain accumulation during the preliminary deformation, hence it was assumed that a variation in the transformation enthalpy during the martensite stabilization effect was caused by the plastic strain that appeared during the deformation. The classical thermodynamics approach for the thermoelastic martensitic transformation was used to confirm this assumption.

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Mechanical and thermal properties of reinforced PMMA resin for interim fixed prostheses with β-pyrophosphate

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Keywords: PMMA, β-pyrophosphate

Interim restorations are essential in fixed prosthodontics as they provide temporary protection of teeth before the permanent restoration. Polymethyl methacrylate (PMMA) is widely used in the fabrication of interim fixed restorations as it is an odourless and tasteless material with a lot of convenient properties such as high impact strength, light weight, shatter-resistance, favorable processing conditions and stable color. Despite the good mechanical properties of PMMA, fractures of interim restorations are very often, necessitating multiple repairs that increase patients' inconvenience and dentists' working time. Many efforts have been made to strengthen PMMA properties by incorporating filler nanoparticles such as alumina, zirconia, silica and nanodiamonds, with promising results. However, prolonged preservation of interim restorations results in increased wear of the resin and consequent damage to the occlusal stability. B-pyrophosphate is considered as a promising material for dental applications and specifically for enamel restoration due to its stability at low pH and the slow wear rate. Due to its biocompatibility and low wear rate, constitutes a good candidate as a reinforcing material of PMMA resins. The aim of this study was to synthesize PMMA/β-pyrophosphate composites suitable for fixed interim restorations and to study their thermal and mechanical properties. Composite PMMA - β-pyrophosphate powders with various amounts of β-pyrophosphate were mixed with PMMA liquid and compact bar specimens were fabricated according to the British standard ISO 10477:2004(E). The structure of the β-pyrophosphate resin was studied by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). The effect of β-pyrophosphate resin on thermal properties of PMMA/β-pyrophosphate composite was investigated using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Also, the three point bending test was used to evaluate the flexural strength of the composites. Loading was applied through an Instron universal testing machine, at a crosshead speed of 1.00 mm/min. SEM investigation was carried out to evaluate the fracture mechanism and crack propagation. Three-point bending test showed a slight increase of the PMMA/β-pyrophosphate composites compared to the pure PMMA at specific β-pyrophosphate percentages. Moreover, thermal analysis techniques showed a remarkable improvement in the composite thermal properties.

Acknowledgments

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Thermal behaviour of the TiO2 powders obtained by microwave-assisted sol–gel method

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Keywords: TiO2 powders, sol-gel method, microwave assisted sol-gel method, thermal behaviour

A comparative thermal analysis study was realized by the Thermogravimetric and Differential Thermal (TG/DTG/DTA) and Differential Scanning Calorimetry (DSC) measurements on TiO_2 system in order to establish the influence of the preparation method on thermal behaviour of powders obtained by the sol-gel and microwave assisted sol-gel methods. Tetraethyl-orthotitanate, titanium tetraisopropoxide and tetrabutyl-orthotitanate were used as TiO_2 precursors, as well as ethanol as solvent and the hydrolysing agent (ammonia containing water) was added dropwise. Based on TG/DTG/DTA results, the temperatures of 450 ^{o}C were chosen for the processing of powders in air. All samples thermally treated at 450 ^{o}C crystallized in a single anatase phase.

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Preparation and thermal study of perovskite based on SrSnO3 doped by Mn-cations

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Keywords: perovskite, pigments, simultaneous DSC-TG, solid state reaction

Perovskite compounds are derived from mineral CaTiO3. This mineral is characterized by orthorhombic structure and has chemical and thermal stability [1].

The general formula of perovskite is ABX3, but most often is described as ABO3 [2]. Classification of perovskite according to valency of the A, B – ions in structure:

- A is ion with 1+ valency (alkali metal) and B is ion with 5+ valency – for example KNbO3;
- A is ion with 2+ valency (alkaline earth metal) and B is ion with 4+ valency – for example SrSnO3;
- A is ion with 3+ valency (lanthanides) and B is ion with 3+ valency (transition metal) – for example LaFeO3 [3].

The main goals of the research are focused on study of formation of perovskite phase by simultaneous DSC – TG analysis and find the appropriate firing temperature. The powders based on $SrSnO_3$ doped by Mn cations were prepared by solid state reaction. Composition of powders is described by general formula $SrSn_{1-x}Mn_xO_3$, where x = 0.1-0.5. The powders were prepared from two initial mixtures reaction ($SrCO_3$, SnO_2, MnO_2) and ($SrCO_3$, SnO_2, $MnCO_3$). The both reaction mixtures were homogenized in a mortar grinder for 10 minutes. After homogenization, the reaction mixtures were in the corundum crucibles inserted into the furnace and were calcined at 950 °C, 1050 °C, 1200 °C, 1300 °C, 1400 °C and 1500 °C for 4 hours (heating rate 10 °C/min). After cooling on the room temperature, the prepared powders were studied by X-ray diffraction analysis (Rigaku Miniflex 600, Japan). The starting materials ($MnCO_3$, $SrCO_3$) and reaction mixtures were characterized by simultaneous DSC/TG analysis (Setaram Labsys Evo, France). The measurement DSC/TG was carried out under an argon atmosphere and in a temperature range 25–1500 °C with heating rate 10 °C/min. After powders application into organic bonding system, colour properties of the powders were measured using a spectrophotometer (Ultra Scan VIS Hunterlab, USA). The colour properties were evaluated in the colour space CIE L*a*b*.

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Synthesis and Characterization of doped BiFeO3 materials

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Keywords: BiFeO3 ceramics, sintering, doping.

Bismuth ferrite is of great technological interest due to their properties and various applications. If modified appropriately, $BiFeO_3$ may exhibit novel physical properties which enrich their functionality. One possible strategy for obtaining improved properties in BiFeO3 is partial ionic substitution. $BiFeO_3$ is one of the rare multiferroic materials with both ferroelectric behaviour (Curie temperature T_C = 830 °C) and antiferromagnetic ordering (Neel temperature T_N = 380 °C) above the room temperature.

In the present work the influence of rare earth elements concentration on $BiFeO_3$:RE ceramics were studied. All ceramic powders were synthesized by conventional ceramic method using high purity raw materials (>99,9%), and subsequently sintered by free sintering and cold pressing method. To analyze the powders and ceramics more the XRD, EDS, SEM, DTA properties were performed.

Thermal analysis of Graphene oxide derivatives

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Keywords: Reduced graphene oxide, XRD, FTIR, Raman spectroscopy

Most applications of graphene depend on its high electrical conductivity and unprecedented structure [1]. However, graphene oxide (GO) is non-conductive because of the extensive presence of saturated sp^3 bonds, the high density of electronegative oxygen atoms bonded to carbon, and other "defects" [1]. Therefore, restoration of the high conductivity of graphene sheet is crucial for its applications. GO was obtained by chemical exfoliation of graphite using the improved Hummers method [2]. In this work we compare the deoxygenation efficiency of GO performed by thermal and chemical ways. Chemical reduction was performed in aqueous suspension with ascorbic acid in highly alkaline medium producing chemically reduced GO (CRGO) [3]. Thermally reduced GO (TRGO) was obtained at 300 °C in argon flow.

The morphology and chemistry of the GO and its derivatives were investigated with powder X-ray diffraction (XRD) and Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR), Raman spectroscopy as well as thermogravimetric analysis coupled with mass spectrometer (TGA-MS), respectively. From these observations we conclude that both the thermal and the chemical treatment of GO result in changing of its morphology and chemical properties. Chemical reduction with ascorbic acid is more effective in the reduction of GO. All the result suggest that CRGO has properties much closer to the graphite.

Acknowledgments

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Thermal stability of indium (III) and dysprosium (III) hydroxides obtained by the sol-gel method

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Keywords: indium, dysprosium, oxide, thermal decomposition

Production of ceramic targets with a high degree of substances homogenization is very important for the films obtaining for sensory and optoelectronics using magnetron sputtering. In our work to obtain a homogeneous mixture of indium and dysprosium oxides for the targets production, the sol-gel method was used. The goal of this work was to study the processes of thermal decomposition of indium and dysprosium hydroxides, synthesized by coprecipitation from chloride solutions, with using thermal and kinetic analyzes. Additionally, the methods of X-ray diffraction and IR spectroscopy were used. The optimum temperature regimes for obtaining ceramic powders for targets have been developed. It was found that the thermal destruction of a mixture of indium and dysprosium hydroxides proceeds in two stages. A smaller number of stages of decomposition of a mixture of hydroxides in comparison with decomposition of each separately indicates the superposition of the processes of thermal decomposition of indium hydroxide and dysprosium hydroxide. The number of thermal effects that characterize thermal destruction does not change, but there is a slight shift in the maximum temperatures of all endothermic effects to the high-temperature region. To a temperature of 280 °C a mixture of indium and dysprosium oxo-hydroxides is formed. Above 280 °C, oxo-hydroxides decompose and at a temperature of 700 °C crystalline indium oxide is formed. The formation of crystalline dysprosium oxide in a mixture with indium oxide is observed at a temperature of 1000 °C. At the same temperature, the oxides interact with each other to form $DyInO_3$. X-ray diffraction analysis suggested the presence of a weakly crystallized oxocarbonate phase of dysprosium. The presence of this phase at the stage of gelation was clearly shown using IR spectroscopy. Decomposition thermograms of a mixture of indium and dysprosium hydroxides and mass spectrometry data observed up to 1400 °C indicated a decomposition of the dysprosium oxocarbonate phase in the temperature range of 1200–1300 °C. The results of scanning electron microscopy indicated a uniform elements distribution in samples of $In_2O_3 – Dy_2O_3$.

Trial of partial Na substitution for Li site in Li_4SiO_4 and CO_2 absorption/desorption property of Li_3NaSiO_4 at various CO_2 partial pressures

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Keywords: Li3NaSiO4, CO2 absorption, thermogravimetry, Ellingham diagram

CO_2 absorption/desorption materials by means of chemical reaction attract interest for solution of global warming. Li_4SiO_4 is regarded as promising CO_2 absorption materials because more than 0.36 g CO_2 can be absorbed per 1.0 g of Li_4SiO_4 and working temperature range is 500~700 °C, which is suitable for CO_2 elimination from exhaust gas from vehicles and factories. However, low CO_2 absorption kinetics of Li_4SiO_4 at CO_2 partial pressure, $P(CO_2)$, of order of 10^{-2} bar should be improved for practical application. Partial substitution of other cation for Li site is probable method for improvement of the absorption property.

Recently, some groups reported that Li_3NaSiO_4 is promising as CO_2 absorbent. However, the other group reported that slight Na substitution for Li site in Li_4SiO_4 improved kinetics of CO_2 absorption, whereas excess substitution decreased the kinetics owing to generation of Li_3NaSiO_4 with no CO_2 absorption. In this study, phase relationship between Li_4SiO_4 and Li_3NaSiO_4 was examined in order to optimize Na content as CO_2 absorbent. Chemical reaction formula of CO_2 absorption of Li_3NaSiO_4 was clarified. The absorption property at various $P(CO_2)$ was also investigated by using thermogravimetry (TG) and compared with that of Li_4SiO_4. The controversy in literatures whether Li_3NaSiO_4 works as CO_2 absorbent or not has been settled.

The specimens with nominal composition of $Li_{4-x}Na_xSiO_4$ (x=0.0-1.0) were prepared by solid state reaction from the mixture of Li_2CO_3, Na_2CO_3 and SiO_2 powders. The mixed powder was pressed into pellet and sintered at 700 °C for 12 h in air on Al_2O_3 plate coated by gold. The obtained phases were analysed by X-ray diffraction (XRD) measurements using RINT-2500 (Rigaku Co., Ltd.: CuKα, 50 kV, 250 mA). CO_2 absorption property was monitored by scanning type thermogravimetry using TG8210 (Rigaku Co., Ltd.). About 30 mg of the powder specimen was set on Pt pan. The heating rate was 5 K/min. The $P(CO_2)$ was controlled by mixing flow rate of CO_2 and N_2 and monitored by CO_2 sensor (Chino Co., Ltd.: MA1001-1P) set at downstream of TG.

Although small peaks identified as Li_2SiO_3 was detected, XRD patterns of $Li_{4-x}Na_xSiO_4$ (x=0.0-1.0) were identified as mixture of Li_4SiO_4 or Li_3NaSiO_4. Intensity of the peaks identified as Li_3NaSiO_4 increased with increasing Na content, indicating existence of miscibility gap between Li_4SiO_4 and Li_3NaSiO_4 without partial substitution of Na for Li site. In order to clarify CO_2 absorption reaction formula of Li_3NaSiO_4, XRD measurement of the specimen after TG measurement in CO_2 flow with heating rate of 5 °C/min to 700 °C and successive cooling at a rate of 100 °C/min was performed. Chemical reaction formula of CO_2 absorption was revealed to be

$Li_3NaSiO_4 + CO2 \leftrightarrow LiNaCO_3 + Li_2SiO_3$ (1).

Figure 1 shows TG-DTG curves of Li_3NaSiO_4 at various $P(CO_2)$. Irrespective of $P(CO_2)$, weight increase, originating from CO_2 absorption according to reaction (1), was observed from about 400 °C. Despite for $P(CO_2)$ range as low as order of 10^{-2} bar, where weight increase identified as CO_2 absorption was small for Li_4SiO_4, maximum weight increase around 10% was clearly observed for Li_3NaSiO_4. This suggests that CO_2 absorption kinetics of Li_3NaSiO_4 is higher than those of Li_4SiO_4 at $P(CO_2)$ range of 10^{-2} bar order. The weight decrease ascribed to reverse reaction of (1) was also observed at every $P(CO_2)$. The temperature of the weight decrease, which can be regarded as equilibrium temperature of eq. (1) at indicated $P(CO_2)$, decreased with decreasing $P(CO_2)$. Ellingham diagram of reaction (1) prepared from Fig. 1 was similar one with that for Li_4SiO_4.

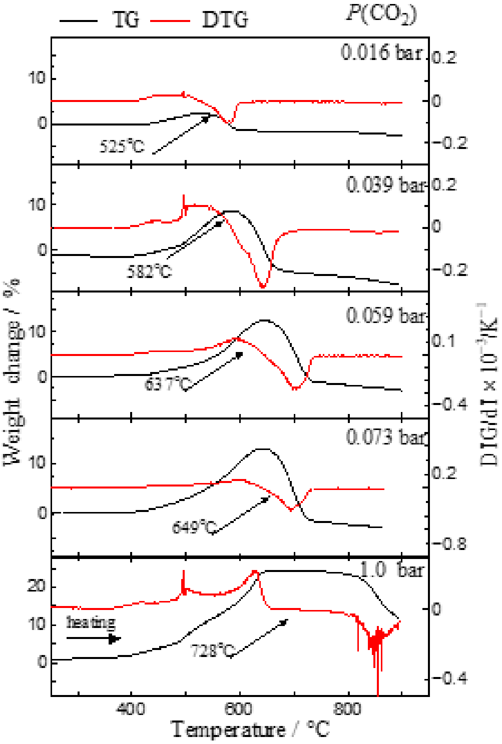

Fig. 1 TG-DTG curves of Li3NaSiO4 at various $P(CO_2)$.

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Crystallization of UHMWPE nanocomposites filled by multi-wall carbon nanotubes

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Keywords: UHMWPE, multi-wall carbon nanotubes, solution blend, crystallization kinetics

In order to study the effect of MWCNTs on the crystallization of UHMWPE, the UHMWPE nanocomposites filled by MWCNTs with high content was prepared by solution method. The non-isothermal and isothermal crystallization of MWCNTs/UHMWPE nanocomposites were studied by differential scanning calorimetry and X-ray diffraction. The results showed that the heterogeneous nucleation of MWCNTs increases the crystallization temperature and crystallinity of UHMWPE filled by MWCNTs below 40 wt % with the increase of MWCNTs content in the non-isothermal crystallization process. However, addition of MWCNTs above 40 wt % reduces the crystallization temperature and crystallinity of UHMWPE with the increase of MWCNTs content. Jeziorny, Mo and Avrami model can describe the crystallization kinetics of UHMWPE nanocomposites filled by MWCNTs with high content. The increase of MWCNTs content decreases the crystallization rate of UHMWPE in the non-isothermal crystallization process. For the isothermal crystallization process, although addition of MWCNTs increases the crystallization rate of UHMWPE, the crystallization rate of UHMWPE also decreases with the increase of MWCNTs content. Above results are discussed based on the combined action of heterogeneous nucleation of MWCNTs and the macromolecular chains of UHMWPE confined on the surface of MWCNTs.

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The Phase Transitions in selective laser melted 18 Ni (300 grade) Maraging Steel

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Keywords: phase transitions, precipitation, dilatometry study, additive manufacturing, maraging steel

Maraging steels have high strength and good ductility, and hence have been broadly used in aerospace and machining areas for many years. Selective laser melting (SLM) is an additive manufacturing printing technology which gives flexibility in geometric design and rapid manufacturing of complicated structures. High-strength 18Ni-300 maraging steel parts were produced by selective laser melting (SLM) additive manufacturing.

The experiments were carried out in an AM125 machine delivered by Renishaw equipped with an Ytterbium fibre laser. Heating and cooling cycles were conducted in the DIL805 A/D dilatometer. For these tests, heating was carried out under low vacuum, approximately 10^{-1} mbar with heating rates of 1, 10 and 20 and 40 °C/s. Changes in length (ΔL) and temperature (T) were measured during heating for each heating rate.

During the heating and cooling thermal cycling, three phase transformations in the maraging steels may be observed: precipitation, martensite reversion and martensitic transformation. These activation energies were determined through the linear thermal expansion coefficient α. Microstructural changes were observed by various techniques, such as, optical microscopy, scanning electron microscopy and X-ray diffraction. The results have shown that the precipitation mechanism for the material in the studied range is by lattice diffusion. The lattice diffusion mechanism in the martensite reversion is influenced heating rate. For higher heating rates the shear mechanism prevails in maraging steels.

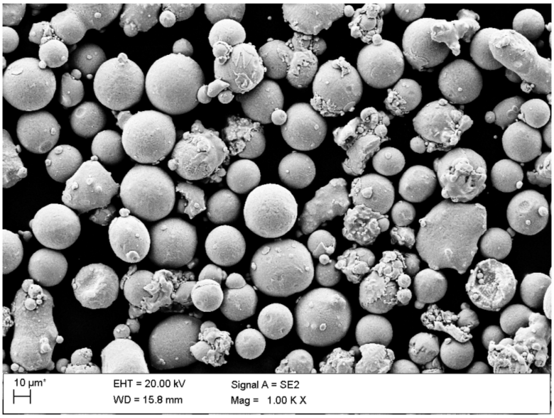

Fig. 1. View of the gas-atomized 18-Ni 300 alloy powder used for the experiments.

Fig. 2. Etched cross-section of the as-fabricated SLM maraging steel observed by OM

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Thermal analysis of porous biomorphic TiC/C composite materials

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Keywords: carbon, DTA, biomorphic, composite, carbotheramal

In this article, synthesis and properties research of biomorphic TiC/C composite material were performed. The basic results of investigations of biomorphic carbon material structures and the method of their infiltration with an organometallic solution of TiO are presented. The obtained porous composite was subjected to the ceramization process to performed carbothermal reduction of TiO/C into the TiC phase. The synthesis process was carried out using the Thermogravimetry TG method and Differential Thermal Analysis (DTA) method for determining the course of thermal processes. The structure of obtained TiC/C material was carried out using light microscopy, Scanning and Transmission Electron Microscopy. The thermal analysis results confirmed the synthesis of a new TiC ceramic phase using XRD and Raman's spectroscopy analysis. The structure and morphology analysis was performed, as well as the specific surface area of the biomorphic material and biomorphic TiC/C composite material after the ceramization process. Moreover, the results of analytical calculations of received reactions were presented and correlated with the obtained results of thermal analysis.

Thermal analysis of porous biomorphic TiC/C composite materials

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Keywords: carbon, DTA, biomorphic, composite, carbotheramal

The ceramic porous materials exhibit many distinct advantages, including hardness, chemical corrosion resistance or high melting temperature find application as filtration component, catalyst or lightweight structural components [1-2]. The production of porous ceramics requires the use of technology that allows the formation of a porous structure. In order to obtain a hierarchical structure, it is required to use a porous structure template with a desired geometry [3]. It is possible to reproduce a porous structure from plant materials exhibit porous structure that allow to produce biomorphic materials [4, 5]. Along with the use of methods of transformation of organic materials and methods for the production of ceramic materials with the sol-gel technique it is possible to manufacture of porous biomorphic materials with a cellular structure of wood [6, 7] .

As the natural material used as a preform in the infiltration process was a pine wood. The dried wood specimens were subjected to pyrolysis in furnace at 800°C for 2h. The resulting carbon char was infiltrated with the sol of titanium isopropoxide (TTiP, $Ti[OCH(CH_3)_2]_4$) and then dried to obtain TiO gel. The preliminary test were carried out to confirm appearance of TiO gel coating and porous structure of carbon char using light microscopy and scanning electron microscopy. The analysis of porous structure confirmed the presence of TiO_x coating on carbon walls (Fig. 1).

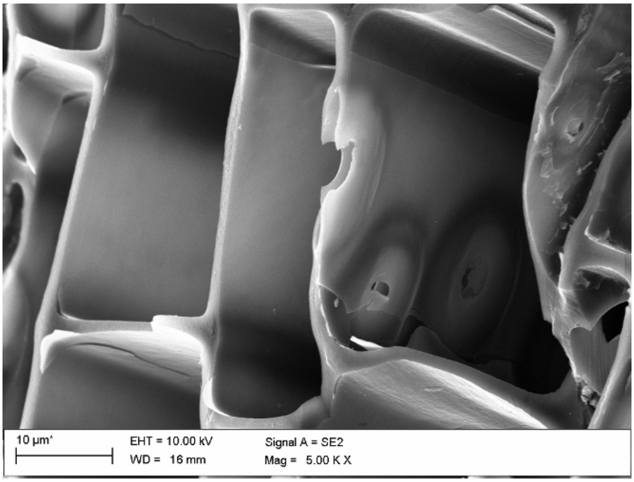

Figure 1. The porous structure of carbon char coating with TiO gel

The infiltration with liquid sol and further calcination of TiO gel allowed to performed carbothermal reduction of oxides in presence of carbon as well preserve porous cell structure of pine wood. However coating of irregular thickness as well the cracks and the enucleation of the Ti-O coating can be seen. Despite infiltration process in low pressure condition and partially degassing of the inner porous structure of carbon char, the thickness of Ti-O coating exhibits uniform distribution. The result may be the hydrophobic properties of the carbon surface, which could decrease wettability of carbon surfaces on the wall of pores. On the other hand, the relatively high viscosity of the Ti-O sol could prevent infiltration of small diameter pores.

The porous carbon char with Ti-O gel were subjected to annealing process in inert atmosphere at 1550°C in order to perform a calcination of TiO-gel and then carbothermal reduction of the TiO/TiO_2 in the presence of carbon to the TiC phase. The interstitial carbide to which TiC belongs should show susceptibility to sintering at a temperature below melting point and depends on stoichiometry of the TiC compound and participation of substrates in carbothermal reduction process [8-11].

The analysis of TiC phase were carried out using light microscopy, Scanning Electron Microscopy, Thermogravimetry (TG) and Differential Thermal Analysis (DTA). The phase composition of porous carbon composite were carried oud using X-ray diffraction.

The analysis of macrostructure of biomorphic carbon char confirm presence of porous structure derived from pine wood. A thorough analysis of the topography of the carbon composite surface confirmed the formation of agglomerates of the new phase. The X-ray analysis results showed that a newly created phase is a mixture of Ti_xO_y and TiC phase (Fig. 2).

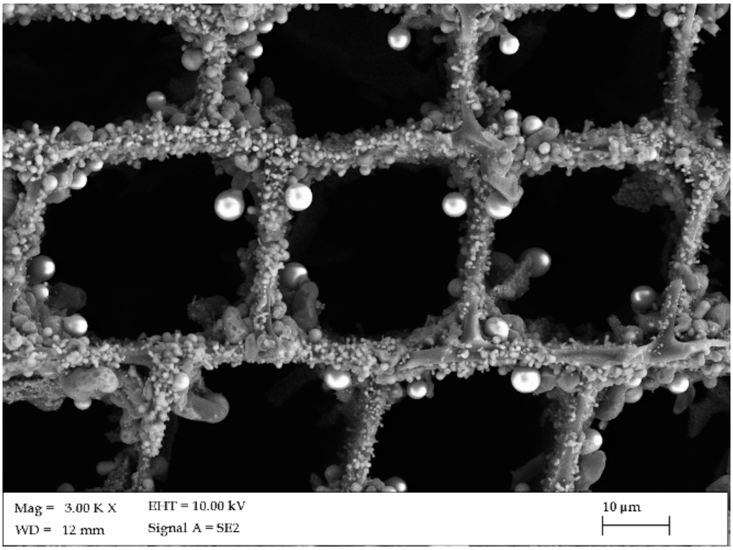

Figure 2. Porous biomoprhic structure of carbon char coating with TiC/TiC_xO_y phase after carbothermal reduction of TiO/C

The incomplete reaction may be related to the non-stochiometric participation of substrates, limitation of substrate contact during carbothermal reduction as well evaporation of reaction products including CO and CO_2.

The result of TG and DTA analysis (Fig. 3) confirm the appearance of numerous phenomena and phase changes occurring during the heating of the TiO/carbon sample up to the temperature of 1500°C. Basis of the TG and DTG analysis graph it is visible significant loss of the sample weight the temperature range 20–100°C which is related to the evaporation of water contained in the sample. The loss of sample mass at temperatures above 200°C may indicate complete conversion of the gel to the amorphous phase of TiO and further TiO_2. The significant mass loss presented by the differential TG chart above 1000°C temperature indicates the occurrence of phase transformations at 1120°C. Moreover, DTA analysis indicate the endothermic reaction above 1200°C related to synthesis of TiC_xO_y and finally TiC phase.

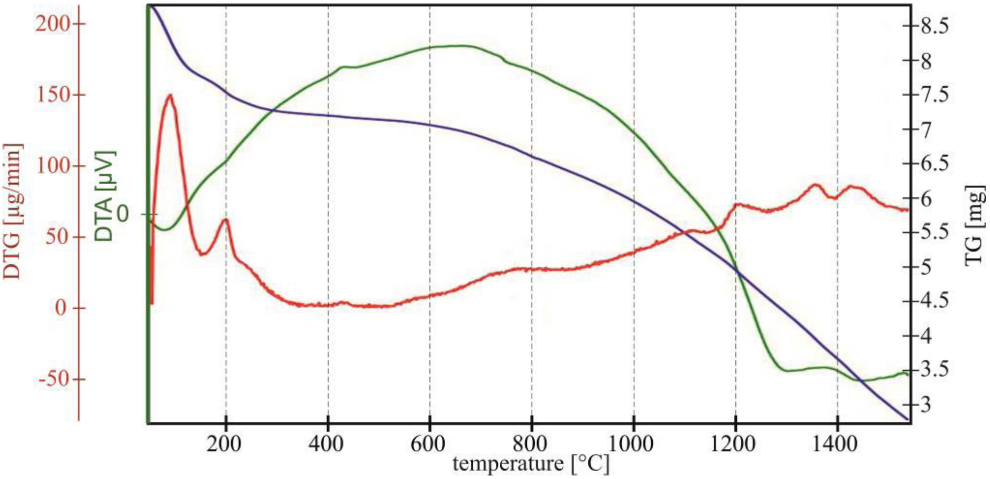

Figure 3. The results of Thermogravimetry and Differential Thermal Analysis of TiO/C porous composite after heating up to 1500°C

The measurement of specific surface area was also preformed in order to determination the influence of temperature on the porosity and surface properties. The carbothermal redictionof TiO/TiO_2 phase in presence of carbon phase significantly influenced the change of specific surface area. BET analysis indicate decrease of amount of micro and mesoporous as well increase the participation of microporosity.

Biomorphic production of TiC composite is difficult due ensuring an adequate participation of substrates during carbothermal reduction with simultaneous preserve the natural structure of wood template.

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Photocatalytic degradation of organic waste in visible light using TiO_2 nanotubes array

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Photocatalytic degradation of organic waste using TiO_2 nanotubes array has been investigated. The phenol was used as organic waste in this research. The Titania nanotubes were obtained by anodization method with 98% ethylene glycol and 0.5%wt NH4F as electrolyte solution at 50 V for 2 hours. The prepared catalysts were characterized by different techniques such as electron microscopy (SEM), X-Ray diffraction (XRD), Fourier transform infrared (FTIR) and UV-vis reflectance spectroscopy (UV-DRS). The effect of pH and initial concentration of phenol has been evaluated. The results showed that the best pH for degradation phenol was obtained at pH 5. In this condition the phenol has been reduced from 40 ppm to 6.9 ppm for 180 min.

Study of different water/dimethylsulfoxide mixtures in confined state

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Keywords: water /dimethylsulfoxide binary mixtures, cryoprotectants, confined state, differential scanning calorimetry, positron annihilation

Dimethylsulfoxide (DMSO) is commonly used as a cryoprotective agent in biology. It is applicable in a mixture with water for long-term storage of cells and tissues at low temperatures. The main problem of cryopreservation is to overcome the phase transition when of liquid water is converted into ice [1]. The formation of intracellular and extracellular ice crystals mechanically damages the membranes of the cells. DMSO affects the rate of water transport from and into the cell, nucleation and growth of ice crystals [2]. DMSO shifts the phase transition of liquid water on ice to lower temperatures, increasing the proportion of non-frozen liquid at low temperatures. However, the process of water vitrification is dominant in this system [3]. The precise knowledge of the cryoprotective mechanism of the DMSO/water mixture at the molecular level is therefore very important for a better understanding of many aspects of controlled cryopreservation. The aim of the performed studies was to find the lowest effective concentration of DMSO because at higher concentrations it has rather undesirable effects.

Liquids in the biological systems are partially located in small volumes. This form of liquid is usually referred to as confined state. Several studies have revealed that numerous physical properties of confined liquids might be modified or even principally changed. This study focuses on the characterisation of DMSO / water mixture in confined state. The SBA15 matrix was chosen as a model system. This material is characterized by a precisely defined fine porous structure.

Mesoporous matrix SBA15 was filled by DMSO/water mixture. The thermal analysis of adsorbed liquid was performed by differential scanning calorimetry (DSC) using power-compensation DSC8500 (Perkin-Elmer) with automatic intra-cooler (200 K). Encapsulated samples and dynamic nitrogen atmosphere were used. The free volume cavity sizes of pure matrix as well as matrix with adsorbed liquid were estimated from the positron annihilation lifetime spectra (PALS) at room temperature.

Acknowledgments
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Enthalpic characterization of activated carbons with different surface chemistry with organic solvents and water

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The immersion enthalpies of modified activated carbons in their chemical surface are determined in benzene, cyclohexane, hexane, ethanol and water. Activated carbons obtained from a granular activated carbon prepared from coconut husk (CAG) were used, which was subjected to oxidation processes with a nitric acid solution and thermal treatment at different temperatures (723 K, 1023 K and 1173 K). Subsequently, the textural and surface chemistry characterization was carried out by Boehm titrations and determination of the pH at the zero load point.

With respect to the chemical characterization, phenolic groups predominate in the original sample and there is a higher total acidity. When carrying out the heat treatment, the quantity of oxygenated groups was decreased and the total basicity increased. In the modification with nitric acid, the presence of the evaluated oxygenated groups increased.

The immersion enthalpies obtained for each of the wet liquids are exothermic. Benzene is the apolar compound that presents the highest enthalpy, followed by cyclohexane and hexane, due to its atomic disposition and interaction with the surface groups of activated carbon; in polar compounds, ethanol presents higher values for enthalpy of immersion with respect to water, due to the ability to interact by the polar and apolar parts of the molecule, its interaction with different oxygenated groups and finally the formation of clusters that favor an increase in solid-solvent energy interactions.

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Influence of freezing and annealing protocols on phases formed in the tert-butanol – water system

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Keywords: Phase transitions, Freezing, Semi-clathrate hydrates, X-ray diffraction, Sublimation behavior, tert-butanol

Freeze-drying (lyophilization) is a drying technology widely used in the pharmaceutical industry [1] to manufacture many injectable products or Zydis® dosage forms (orally dissolving tablets). Water is the most commonly used solvent in the freeze-drying method. However, scarce solubility of some hydrophobic and poorly water soluble drugs severely limits the application of freeze-drying using aqueous solutions, so that pure organic solvent or organic co-solvent / water formulations have also been investigated in recent years [2-5]. Using organic – water co-solvent systems in the freeze-drying process facilitates manufacture of the stock solution by increasing the wettability and solubility of APIs. This allows one to increase sublimation rates, decrease reconstitution times, and improve freeze-dried product stability. Of common organic – water co-solvent systems, tert-butanol (TBA) – water system is studied in relation to increasing the efficiency of freeze-drying in pharmaceutical industry. The main advantages of TBA – water system include a low residual solvent contents, a low toxicity of the residual TBA, high eutectic melting temperature (easy freezing / sufficiently high shelf temperature during primary drying) [3, 6].

Here we report the X-ray diffraction and thermal analysis studies which show a strong impact of the freezing protocol on the phases formed in the TBA – water system; up to 3 different phase states can be realized depending on freezing protocol used. We add surprising new data to the phase diagram of this previously repeatedly studied system and show that decahydrate [7] forms only on high cooling rates (>10°/min). The decahydrate begin to decompose at temperatures above -40°C to ice I*h* and heptahydrate. In particular, we show that – whichever cooling rate is used – the heptahydrate (H2) cannot be obtained in its "temperature-composition" stability region. Depending on the cooling rate, either ice I*h* and deca- (H3) or di- (H1) hydrates are crystallized. X-ray diffraction studies of frozen and annealed samples performed at different temperatures confirm anomalous stability of the dihydrate in the "temperature-composition" stability region of heptahydrate. The substitution of sublimed H1+I*h* for H2+I*h* leads to both a reduction of primary drying time and a significant increasing in specific surface area of the trehalose freeze-dried cakes. This finding is of great importance for practical applications, including pharmaceutical/biopharmaceutical drug formulation.

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Approaches for better thermal analysis – activities of the standardization working group of JSCTA (Japan Society of Calorimetry and Thermal Analysis)

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Keywords: standard reference materials, education, DSC, TMA, RRT

The Working Group (WG) on Standardization of Japan Society of Calorimetry and Thermal Analysis (JSCTA) was established on 1999, and coined problems on the standardization of thermal analysis in the 31st Workshop held in 2000. Since then, challenges for solving two problems on standardization have been made; one is related to the certified reference materials, and the other concerns methodology. In 2003, the WG focused on the calibration of differential scanning calorimeters (DSCs), particularly the temperature calibration, and in order to realize the present status, enquiries were made to thermal analysis specialists and to the general users of thermoanalytical instruments. Furthermore, pure In, Sn, Pb, and Zn were prepared and put to round robin test (RRT) for evaluation as calibration standards. As a result, problems related on the user knowledge on instrument calibration, poor availability of the reference materials, cost and time-consuming calibration, uncertain calibration procedure, etc. have been realized. In 2005, based on the results, introductory practice course for understanding the importance of instrument calibration was incorporated for the first time in the three-day training short course. Since then, basic course for the beginners is held every year.

During 2007–2008, RRTs on the validation of cyclohexane as a reference material for the calibration of DSC, and of silicon single crystal and glass-like carbon (GLC) as a reference for measuring thermomechanical properties were carried out. These efforts resulted on the establishment of 3 certified reference materials (CRM) now available from National Metrology Institute of Japan (NMIJ) (Table 1).

The objective of this paper is to report and discuss on the challenges and the recent activities of Working Group (WG) on Standardization of JSCTA.

Table 1 Reference materials now available from NMIJ

Thermal Properties	Reference Material
Thermal Expansion	Silicon Single Crystal: 1101-a, 5803-a
	Glass-like Carbon: 1102-a, 1104-a
Specific Heat Capacity (low temperature)	Silicon Single Crystal: 5806-a
Phase transition	Cyclohexane for thermal analysis: 5401-a

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Studies of structural and thermal behavior of $Y_{1-x}Bi_xFeO_3$ ($X=0.00, 0.01, 0.03$ & 0.05)

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Keywords: Perovskite, Weight loss, Specific Heat, Enthalpy

Bismuth Substituted Yttrium orthoferrite nano powders have been prepared by Sol-Gel route by setting the pH value at 9 on pH scale. The room temperature X-ray diffraction patterns confirm the single phase orthorhombic symmetry with space group Pnma. The Rietveld Refinement fitting through FullProf program provided various geometrical and lattice parameters with very low $\chi 2$ and GOF value. The particle size (D) has been measured using Scherrer and Williamson Hall methods. 2 and 3-Dimensional surface morphology have been collected using atomic force microscopy (AFM) which also supports the particle size to be of the order of nano sized. The thermal behaviour have been studied using DTA/TG analyser in the temperature range from RT to 1223K which shows sluggish transition near Neel Temperature (644K) in heating as well as in cooling cycle. These sluggish transitions were verified using DSC measurement technique in the temperature range from RT to 823K which is in good agreement with each other and explains the magnetic transition. The results are discussed in detail.

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Hot deformation behavior of a heat treated AlMg3 alloy

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Keywords: Aluminium, heat treatment, microstructural evolution, activation energy

Plastic deformation behaviour of aluminium alloys at low strain rates has continued to attract research interest in order to understand their deformation and mechanical properties at various rates of loading. AlMg3 aluminium alloy is an aluminium alloy with magnesium and traces of silicon. It is highly resistant to attack by seawater and industrial chemicals. AlMg3 alloy that combine good strength, extrudability, favourable corrosion resistance with low cost have recently been used for automotive body sheet panel for weight saving, furniture, architectural facing and structures and transport vehicle frames. However, this is somewhat limited by reduced formability in these alloys, nevertheless both stiffness and mechanical properties are sufficiently high. It is important to study the deformation behaviours of AlMg3 aluminium alloy for optimizing the processing performance and controlling the internal microstructure evolution by using hot deformation behaviour.

The hot deformation behaviour of the AlMg3 alloy in a heat treated state was investigated by compression test in the temperature range of 100 ºC–400 ºC and a strain rate in the range of 10^{-4} s^{-1} to 10^{-2} s^{-1} using dilatometer DIL 805A/D equipped with accessory attachment deformation allows the process to execute thermo-plastic in vacuum and inert gas atmosphere. Associated microstructural changes characteristics of examined alloy were studied using a light and electron microscopy.

Application of thermal analysis to control the solidification pattern of ductile iron casting in coated mould with sulphur or oxygen content

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Keywords: Thermal analysis, solidification cooling curves, eutectic undercooling, ductile cast iron, mould coating, degenerated graphite surface layer, structure

Ceramic moulds used in metal castings production are usually coated in order to control the metal-mould chemical interaction and to decrease the casting surface roughness, respectively. In Mg-treated iron castings, the coating is also important to control the graphite degeneration process in the surface layer. The surface layer with degenerated graphite causes stress raisers in the casting, similar to a notch, so all the properties are reduced, especially the fatigue limit and impact resistance. The applied coating on the active surface of the mould in order to improve the casting surface quality also influences the solidification characteristics of the casting body.

The main objective of the present paper is to evaluate by thermal (cooling curve) analysis the solidification pattern and the occurrence of the layer of degenerate graphite at the surface of ductile iron castings, with and without mould coating, including sulphur or oxygen, and different agents (carbonic material, iron powder) to blocking their diffusion into the iron melt. Thermal analysis of the solidification process is recorded in standard ceramic cups [0.75cm cooling modulus]. The obtained cast samples are used for structure evaluation [metal matrix and graphite parameters], in the superficial layer and the casting body.

It is found that the mould coating materials influence not only the occurrence and the thickness of the un-desired surface (skin) layer but also the parameters of the solidification cooling curves, during eutectic reaction and up to the end of solidification, in the same or in an opposite way. Sulphur presence in the mould coating will promote higher skin thickness comparing to oxygen, while carbonic material or iron powder supplementary addition decreases these un-desired effects, but the solidification undercooling comparing to the equilibrium system is prominently increased.

Investigation of phase state of water adsorbed on poly (acrylic acid) hydrogel

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Keywords: poly (acrylic acid) hydrogel, dehydration, phase state, activation energy

Hydrogels are hydrophilic macromolecular networks which are able to adsorb large amount of water, but rather swell than dissolve in it. State of adsorbed water has been analysed in literature by various techniques: thermogravimetric analysis, calorimetry, dielectric relaxation spectroscopy, NMR, etc[1]. This led us to the situation where state of water is characterised by different names depending of the methodology and thus, there are: free and bound water; freezable and non-freezable water; mobile and immobile water, etc. With the aim to take more global picture and to find more generalised description of phase state of adsorbed water in hydrogels, our objective is to analyse phase state of water adsorbed within poly (acrylic acid) hydrogel thought two different perspectives, by thermogravimetric analysis and by molecular simulation. Poly (acrylic acid) hydrogel was synthetized using the procedure given in [2] and its basic structural properties were determined. Isothermal thermogravimetric curves have been recorded in temperature range from 306 K to 361 K. Thermogravimetric curves were fitted by linear combination of logistic functions. Dependence of activation energy on dehydration degree was determined by isoconvesional method for whole dehydratation process. By knowing relations between parameters of logistic function and kinetics parameters activation energies and pre-exponential factors were calculated for dehydration components (described by certain logistic function) [3]. Structure of poly (acrylic acid) hydrogel with different swelling degrees and with experimentally obtained basic structural properties has been simulated by hybrid Monte Carlo-Molecular dynamic approach, which allows faster optimization due to the easier diffusion of water molecules through pores of hydrogel. Using energy decomposition scheme proposed by Rahm and Hoffmann for each of the swelling degrees energy of averaged bond between molecule of water and other molecules was calculated and bond was characterised by descriptors developed within this scheme [4]. Using both approaches discussed were changes in: number and energy of averaged H-bonds, mobility of water molecules and phase state of water with dehydration.

Acknowledgments

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Application of TG and Q-TG thermogravimetry for study of physicochemistry properties of biomaterials

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Keywords: TG and Q-TG thermogravimetry, properties of adsorbed liquid films, advanced technology materials, starch biopolymers, AFPs proteins

The thermal analysis techniques have been adopted to study the liquid/solid systems [1,2]. The first measurements were carried out ca. 40 years ago by means of derivatograph OD-103 (MOM, Hungary) [3]. The samples (adsorbents, minerals, advanced technology nanomaterials, composites, biopolymers, plants) were saturated and/or wetted with polar and nonpolar liquids. Thermodesorption processes of liquids from solid surfaces were registered and used in practical calculations of the such parameters as adsorption capacity of materials, thickness of liquid films, pore volume and size, pore size distribution function, fractal coefficients, enthalpy, entropy, activation energy, film pressure, desorption energy distribution function [4].

The TG and Q-TG mass loss curves as well as the first derivatives of mass loss curves, DTG and Q-DTG, with dependence on temperature and time under classical and quasi-isothermal conditions have been obtained using Q-1500D derivatograph connected with computer system and controlled by *Derivat* program. The physicochemical properties, e.g. thermal stability and decomposition of starch biopolymers and antifreeze proteins (AFPs) in plants were investigated. Unique water properties of the water adsorbed on pure and modified surfaces were also obtained. The results have been compared with similar parameters from sorptometry, porosimetry and AFM data and a good agreement was verified.

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Characterization of thermal behavior of pure and doped hydroxyapatite

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Keywords: precipitation, hydroxyapatite, doping, thermal stability, XRD, SEM

The term "apatite" applies to a group of compounds with a common formula in form $M_{10}(XO_4)_6Z_2$, where Z- may be typically OH^-, F^-, Cl^-. Hydroxyapatite (HAP) has the molecular structure of apatite, where M is calcium (Ca^{2+}), X is phosphorus (P^{5+}) and Z is the hydroxyl group (OH^-) [1]. Hydroxyapatite (HAP) is a stable apatite compound and has been used widely due to its similarity to human bone composition, bioactivity, and biocompatibility [2]. In order to improve some of the properties of HAP, such as osseointegration and implantation, HAP samples were doped with small amounts of additives (e.g. magnesium, zinc, aluminum, strontium) [3]. These smaller groups and elements play the main role in the physiological reactions associated with bone metabolism [4]. The general form of HAP is the hexagonal crystal structure, $P6_3/m$ space group, with Ca/P ratio 1.67 [5]. The optimum Ca/P molar ratio must be 1.667. However one of the main problems related to HAP processing is the low stability of HAP at temperatures near to the sintering range, which is attributed to deviations from the ideal Ca/P ratio [6]. In addition, a lot of factors contribute to complicating the image: sample structure, particle size, purity, powders surface condition, and particles aggregation can support undesirable decompositions and phase transitions [7]. In consequence, several compounds can be formed such as oxyapatite (OAP), oxyhydroxyapatite (OHAP), β-tricalcium phosphate (β-TCP), calcium oxide and tetracalcium phosphate (TTCP) [8]. The formation of β-TCP ($Ca_3(PO_4)_2$) as the most probable phenomenon in the decomposition process highlights the importance of the Ca/P ratio in the control of HAP stability [7]. The main objective of this study is to determine suitable synthesis conditions for the formation of pure and doped hydroxyapatite phases with the possibility of substitution of Mg^{2+}, Zn^{2+}, Al^{3+}, and Sr^{2+} ions. Another aim is to investigate the influence of substitution elements to the structure of hydroxyapatite, to evaluate their adaptation in structure and to investigate their thermal behavior. The synthesized powders were characterized by X-ray diffraction (XRD, Rigaku Miniflex 600) in order to identify the phase composition and crystallinity; the morphology of powders was investigated by scanning electron microscopy (SEM, JSM-5500 LV) and the thermal behavior of powders was explored by thermal analysis using the STA 449C Jupiter (NETZSCH, Germany) which allows simultaneous registration of the thermoanalytical curves TG and DTA.

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Bi-doped $PrFeO_3$ prepared using mechanical activation

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Keywords: Perovskite, mechanical activation, colour properties, thermal analysis

Orthoferrites with chemical formula $LnFeO_3$ (Ln = lanthanides) represent a special subgroup of perovskites. They are studied mainly due to excellent properties for example as chemical sensors for detection of humidity or alcohol [1]. Mechanical activation could be one of possible methods that would help to improve the reactivity of the starting materials. This operation is associated with the use of external mechanical energy, usually by means of a very intensive grinding. The aim of the activation is to accumulate energy in the form of defects or other structural modifications of a solid, which makes it possible to decrease the activation energy or improve steric conditions for its subsequent chemical transformations [2].

In this work, $PrFeO_3$ pigments doped by bismuth were prepared and the mechanical activation was used as a pre-treatment of starting materials. Fe_2O_3, Pr_6O_{11} and Bi_2O_3 of analytical purity were used for synthesis. The starting mixtures corresponding to chemical composition $Bi_xPr_{1-x}FeO_3$ (x=0-3) were in stoichiometric ratio homogenized in agate mortar. For mechanical activation the planetary mill Pulverisette 5 (Fritsch, Germany) was used. Conditions of this pre-treatment were following: grinding material – agate balls with diameter 10 mm and agate bowl; speed rotation – 250 rpm; time of activation – 6 hours; ball-to-powder mass ratio – 20/1. Thus prepared initial mixtures were calcinated at 1000°C and 1100°C for 3 hours with a heating rate 10°/min.

For characterization of the thermal behavior and formation of the orthoferrites the thermoanalytical methods were used. The thermal analyses of the mixtures $Bi_{0.1}Pr_{0.9}FeO_3$ and $PrFeO_3$ pre-treated by mechanical activation were performed by STA 449C Jupiter (Netzsch, Germany) allowing the simultaneous registration of the thermoanalytical TG and DTA curves. The initial mixtures were studied in the temperature region 25-1000°C with the heating rate 10°/min. Prepared samples by heating process were subsequently investigated as inorganic pigments. Phase composition of orthoferrites was verified by X-ray diffraction analysis (Miniflex 600, Rigaku, Japan) and the phase identification of powders was achieved with program that using matching of the diffraction patterns with data by the ICDD-PDF2 database. The thermal stability was determined by heating microscope with automatic image analysis EM 201-12 (Hesse-Instr., Germany). Main attention of work was concentrated on study of influence of mechanical activation on colour and optical properties. The colour properties were investigated for powder samples and after application into organic binder. The equipment ColorQuest XE (HunterLab, USA) was used for this research. The particle size of prepared compounds was measured by the device Mastersizer 2000/MU (Malvern Instr., UK). The results of this analysis pointed out on unfavorable particle size distribution. The d_{90} values of orthoferrites ranged from 19 μm to 57 μm. Therefore, the powder samples were milled to improve their particle size.

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The effect of prolonging sintering time on dielectric and electric properties of six-layered aurivillius compound $Bi_7Fe_3Ti_3O_{21}$

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Keywords: multiferroics materials, Aurivillius phases, $Bi_7Fe_3Ti_3O_{21}$, dielectric properties, impedance spectroscopy

A number of interesting studies confirming the influence of sintering temperature on the dielectric properties [1,2,3,4], optical properties [5] and structural changes [6,7] have been reported for conventional ferroelectrics such as $BaTiO_3$ or PZT. The influence of different sintering time effect on characteristics of multiferroics in the Bi-Ti-Fe-O system known as Aurivillius phases with the general formula $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ has not been investigated yet. The various ways and conditions of preparing and sintering these materials play a crucial role on the microstructure, dielectric and electric properties. The main purpose of this work is to learn the effect of sintering time on the microstructure, dielectric and electric properties of six-layered $Bi_7Fe_3Ti_3O_{21}$ (BFT) compound. In addition to the scanning electron microscope images and the temperature characteristics of dielectric permittivity and dielectric loss tangent as a function of the sintering time, the results of impedance spectroscopy will be presented. The last one allowed to determine influence of the extending of the sintering time on the electric parameters of the grains and grains boundary (electrical resistance, conductance and capacity). A equivalent circuit has been proposed.

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Optimization of supercritical carbon dioxide dyeing for plastic buttons

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Keywords: Supercritical CO2, Dyeing, Plastic Button, Acrylic, Casein, Polyester, Nylon, Multiple regression

Conventional wet dyeing processes simultaneously produce a large amounts of wastewater containing dyestuffs with chemical auxiliaries and require a considerable energy for drying after dyeing. Besides, the residual dye remaining after the processing cannot be easily separated and recycled. In order to improve these problems from the standpoint of environmental aspects, energy conservation, and 3R (reduce, reuse, and recycle) technology, supercritical carbon dioxide (scCO_2) dyeing process has newly developed instead of the conventional wet dyeing. Carbon dioxide (CO_2) is nontoxic, harmless, non-flammable, and low price and has the critical temperature (T_c = 31.1 ºC) and the critical pressure (P_c = 7.38 MPa), which can be brought into a supercritical state easily. The scCO_2 dyeing process can save a lot of the consumption energy and cost for no waste water treatment as well as no drying process. After dyeing treatment, residual dyestuff and 90%-CO_2 used can be recycled and reused. The main advantages of scCO_2 to water are due to the fact that scCO_2 molecules swell the buttons and diffuse dye molecules through the polymer by the high diffusivity and low viscosity and surface tension of scCO_2. Moreover since the density of scCO_2 can easily be controlled by operating temperature and pressure, it is easy to separate the dye dissolved in scCO_2 from the dyeing medium. So, scCO_2 dyeing process is a green and environmental friendly process, and energy saving one that can meet sustainable development.

We newly designed and constructed an apparatus for dyeing of plastic buttons of acrylic, polyester, nylon, and casein in supercritical carbon dioxide. We carried out the dyeing the plastic buttons over the temperature ranges of 40 to 55ºC and pressures of 8 to 14 MPa for acrylic, 10 to 16 MPa and 110 to 125 ºC for polyester, 21 to 29 MPa and 110 to 130 ºC for nylon, and 8 to 14MPa and 80 to 110 ºC for casein. And we examined the dyeing color depth of the buttons measured by a spectral color difference meter. The K/S values of the dyeing buttons evaluated by Kubelka-Munk equation were used to correlate the operating valuables of temperature, pressure, and dyeing treatment time for dyeing of plastic buttons of acrylic, polyester, nylon, and casein in supercritical carbon dioxide. Moreover, we proposed several correlation models to estimate the K/S values for acrylic, polyester, nylon, and casein buttons by the multiple regression analysis. We could formulate a model to correlate the experimental K/S results with the solubility of dye in in supercritical carbon dioxide y, temperature T, and dyeing treatment time for the plastic buttons. The correlation coefficients determined by the multiple regression analysis were 0.679 for acrylic buttons, 0.617 for polyester buttons, 0.945 for nylon buttons, and 0.543 for casein buttons. Good agreement between the experimental and calculated results could be obtained from the correlation model. The optimum

K/S values estimated from the model were 40 ºC, 14 MPa, and 30 min for acrylic, 125 ºC, 12 MPa, and 60 min for polyester, 130 ºC, 29 MPa, and 80 min for nylon, 110 ºC, 14 MPa, and 20 min for casein. Finally we confirmed that the optimum K/S values estimated from the multiple regression model with a higher determination coefficient were in satisfactorily better agreement with those obtained by the experimental design method reported previously.

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Synthesis and thermal investigation of vanadium doped ZnO nanopowders obtained by sol-gel method

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Keywords: doped zinc oxide, sol-gel method, thermal analysis

Zinc oxide has been intensely investigated by researchers in pure and doped form. ZnO is an n-type semiconductor with large exciton binding energy of 60 meV and direct energy band gap of 3.36 eV. Doping it with different metal ions introduces outstanding changes in the structural, electrical, optical, and magnetic properties which encourage their use in various applications, such as: TCOs, sensors, microelectromechanical and piezoelectric devices. Vanadium is a promising element in improving the electrical conductivity and the piezoelectric properties of ZnO. This paper reports the synthesis and properties of nanocrystalline powders of V-doped ZnO obtained by sol–gel method, using zinc acetate dehydrate and vanadium oxide acetylacetonate as precursors. The influence of the vanadium content (1, 2, 5%) on the thermal behavior of the as-prepared gels was determined by thermogravimetric and thermodifferential analysis (TG/DTA). The thermal treatment of the samples was established based on the results obtained by thermal analysis. The properties of the gels and of the resulted powders were studied by Fourier transform infrared spectroscopy (FT-IR). X-ray diffraction (XRD) and scanning electron microscopy (SEM). The studied compositions are of interest for possible applications in microelectronic devices.

Advances in a new multicomponent crystal system: synthesis, structure, thermal and kinetic investigations and biological activity

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Keywords: multicomponent organic crystal, thermogravimetric analysis, X-ray diffraction, plant growth regulatory activity

Multicomponent organic crystals built from acid-base complexes play an important role in solid state chemistry, agriculture and pharmaceutical industry. Desired properties as improvement of solubility, bioavailability and stability are main motivations for producing multicomponent organic salts. This study comes to complete our previous researches focused on the thermal analysis and properties of alkanolammonium benzoates [1-3]. Here, the synthesis, thermal and kinetic investigations, X-ray crystallographic structure and the biological activity of methylethanolammonium 4-nitrobenzoate (MMEA4NB) in *Solanum lycopersicum* L are provided. The new compound was obtained in excellent yield, shorter reaction time and room temperature. Thermal stability and thermal decomposition were studied in dynamic air atmosphere by means of simultaneous thermogravimetry – differential thermal analysis – derivative thermogravimetric (TG-DTA-DTG) techniques (Fig.1). Proton transfer and hydrogen bonding in the organic salt were elucidated and confirmed by infrared spectroscopy and single crystal X-ray diffraction (XRD). Single crystal XRD reveal that the crystal belongs to the triclinic system with the centrosymmetric space group P-1: a=7.1554(7), b=7.9829(7), c=10.4431(9) Å, α=76.055(7), β=82.422(7), γ=86.246(7)°. Two protonated methylethanolamine cations interconnect by N–H···O and O–H···O hydrogen bonds with two 4-nitrobenzoate anions in a tetramer (Fig.2), which is further assembled via $\pi\cdots\pi$ and C-H···π interactions, thus forming a 2D supramolecular layer. Phytotoxicity test indicates that the new compound has plant growth regulatory activity in *Solanum lycopersicum* L, and this result may open new perspectives in plant growth regulators area.

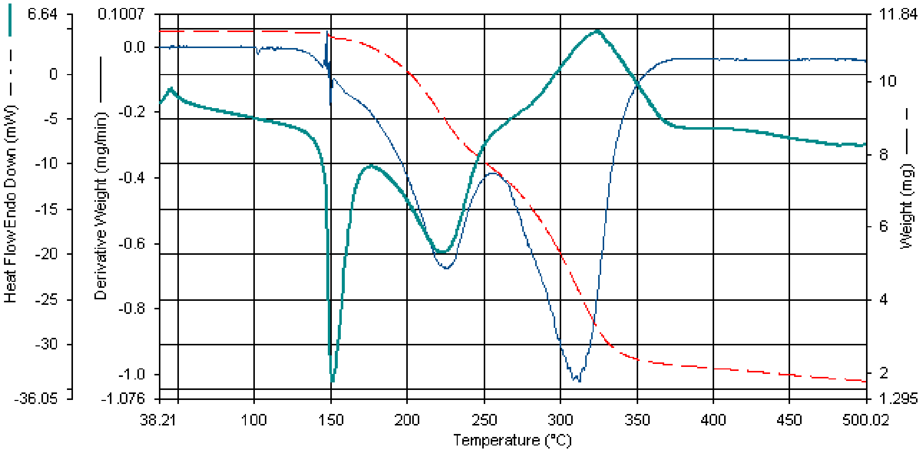

Figure 1. Thermogravimetric curves of MMEA4NB at heating rates of 10 ºC min^{-1}, in air

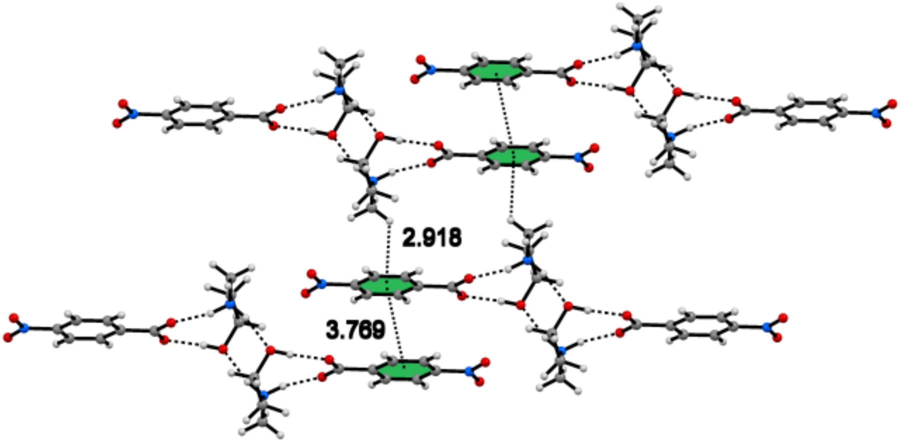

Figure 2. Fragment of 2D supramolecular layer

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Dielectric anomaly of ionic liquid, $(C_8mim)BF_4$, observed on stepwise heating: equilibrium time dependence

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Keywords: ionic liquids, phase transition, thermal history

The physicochemical properties of ionic liquids exhibit peculier properties that are not found in ordinary molecular liquids since the molecules interact with both van der Waals and Coulombic interactions. These interactions provide thermal hysteresis on their phase behavior depending on the rate of the temperature change. The ionic liquid, 1-octyl-3-methylimidazolium tetrafluoroborate, abbreviated as $(C_8mim)BF_4$, is vitrified at the typically high scanning rate of DSC 5 K min^{-1}[1], but application of the intermittent heating at the relatively low scanning rate about 15 mK min^{-1} in the average induces the phase transition from the liquid to liquid crystal[2]. The very slow rate for the phase growth might be affected by the thermal history at around the glass transition temperature, T_g = 187 K. However, it is unclear in detail how the phase behavior changes depending on the scanning rate. In this study, the dielectric spectroscopy was performed on $(C_8mim)BF_4$ to investigate how the phase behavior during heating process depends on until which temperature the sample is cooled from the room temperature, that is the initial temperature, T_{ini}, for heating measurement. Furthermore, the dependence of the equilibration time, t_{eq}, which means how long the sample is isothermally kept for recovery of the thermal homogeneity after heating, was also examined. As shown in Fig. 1, after cooling from 250 K to T_{ini} = 180 K at a cooling rate of 1 K min^{-1}, the temperature was step-wisely increased from 180 K to 250 K by 1 K. The dielectric constant was determined on the isothermal condition at each temperature after having undergone the equilibration times, t_{eq}, followed by the intermittent heating. Fig. 2 shows the dielectric constant on the heating process with reference to the cooling ones. The measurements were performed with t_{eq} = 300, 600, 900, 3000 s for equilibration as the reference to the ones with t_{eq} = 10000 s previously measured by Takamatsu [2]. In the cooling process, the dielectric constant continuously decreases as the temperature decreases. On the other hand, in the heating process the dielectric anomaly was observed when measured with the intermediate equilibration time. With the equilibrium time in between 600 s and 900 s, a sharp peak was shown at 244 K, suggesting the emergence of a noble metastable phase.

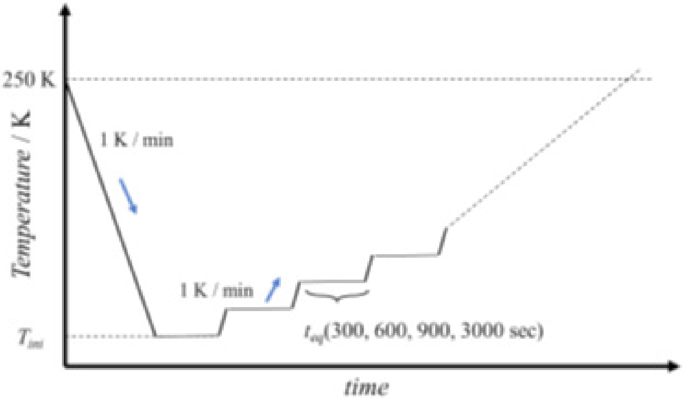

Fig. 1 Temperature profile for the dielectric measurement: After cooling from 250 K, the temperature was raised by 1 K from 180 K. The dielectric permittivity was determined followed by waiting the equilibrium time, teq, after each stepwise heating. The teq was taken to be 300, 600, 900, 3000 s.

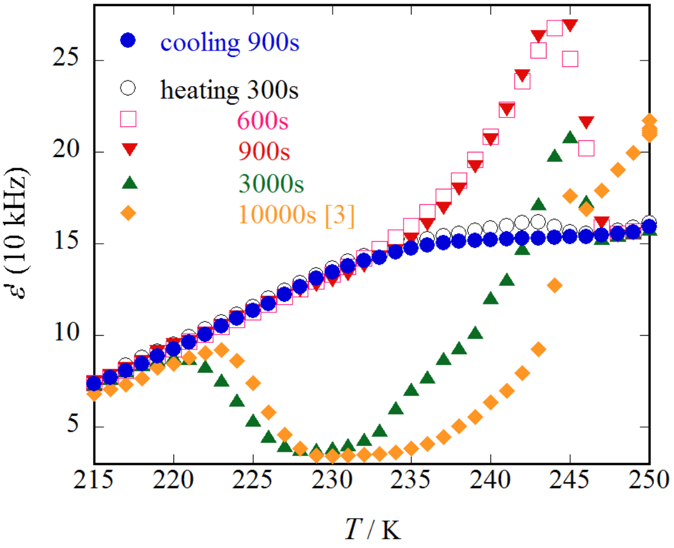

Fig. 2 Temperature dependences of the dielectric permittivity measured with different equilibrium times teq: The frequency f is 10 kHz. The closed circles show the values measured on cooling and the closed diamonds show the plots as a reference measured with teq = 10000 s by Takamatsu et al. [2].

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Thermal and Relaxation Behavior of the ice in bovine serum albumin solution

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Keywords: Protein hydration, Ice XI, Glass transition

A lot of forms of ice exist on the earth as a continent, a particle of cloud, snow, glacier etc. Ice is not only important for the lives on this planet, but also intriguing from the viewpoint of physics, chemistry and biology. since plenty forms of ice crystal structure have been found to exhibit polymorphism in such a low molecular material. Depending on the conditions where water exists, the structural form of the ice varies. The structural difference is supposed to be attributed to the 3-diimensional network due to the hydrogen bond. So far, it is not understood how the hydrogen bond network changes depending on the circumstances around the water. Previously, adiabatic calorimetry indicated that the water molecules hydrated to a protein, bovine serum albumin abbreviated as BSA, molecule forms three different types of hydrogen bond structures when the hydration degree is lower than 0.43h (water-g/protein-g) [1]. When the hydration degree is higher than it, the part of water molecules are well-known to be crystalized. However, it is not understood in detail how the hydrogen bond structure varies and the dielectric behavior depending on the scanning rate.

In this study, adiabatic calorimetry was performed to investigate the thermal behavior of the water molecules hydrating to the BSA for higher hydration degree than 0.43h. It was confirmed that the ice XI structure within the protein solution. The ice XI structure has typically been found in NaOH doped ice, and hence BSA molecules might play such a dopant. Furthermore, the dielectric spectroscopy showed that multi relaxation behavior including ice, glassy water, protein side and main chains.

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Thermal analysis of EN AW-AlCu$_4$Mg1(A) alloy matrix composite reinforced with Al$_2$O$_3$ particles

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Keywords: Surface treatment; Differential Scanning Calorimetry, Fibre laser, Silver alloys; Laser feeding, Metal powder

The aim of this paper is to present modern manufacturing method of production and compare the thermal, mechanical, corrosion resistance properties as well as microstructure of composite materials with aluminium alloy matrix reinforced by Al$_2$O$_3$ particles. The material for investigation was manufactured by the method of powder metallurgy (consolidation, pressing, hot concurrent extrusion of powder mixtures of aluminium EN AW-AlCu4Mg1 (A) and ceramic particles Al$_2$O$_3$) and pressure infiltration of porous performs by liquid alloy. The amount of the added powder was in the range of 5 mass.%, 10 masss.% and 15 mass.%. Powders of the starting materials were wet mixed in the laboratory vibratory ball mill to obtain the uniform distribution of the reinforcement particles in the matrix. The mixed powders were then dried in the air. The components were initially compacted at cold state in a die with the diameter of Ø 26 mm in the laboratory vertical unidirectional press – with a capacity of 350 kN. The selected compacting load was sufficient to obtain prepregs which would not crumble and at the same time would not be deformed too much, which would also have the adverse effect on their quality, as the excessive air pressure in the closed pores causes breaking the prepreg up when it is taken out from the die. The obtained PM compacts were heated to a temperature of 480-500℃ and finally extruded – with the extrusion pressure of 500 kN.

Concerning the thermal properties especially the linear thermal expansion coefficient was measured, as well as the dilatometric change of the sample length was analysed. Based on microstructure investigation a precipitation hardening process was determined which causes corrosion resistance growth of the investigated materials. The highest corrosion resistance compared with the matrix (corrosion wear after the test in 3% NaCl water solution) is characteristic of the composite materials reinforced by 5 and 10% Al$_2$O$_3$, with the corrosion rates of 0.002 mm/year and 0.013 mm/year respectively. The corrosion rate for the composite with 5% portion of the Ti(C,N) particles is 0.021 mm/year. The worst corrosion resistance is characteristic of the composite material reinforced with the BN particles. It was also demonstrated that the microstructure of the extruded composite materials based on the EN AW-Al Cu4Mg1(A) alloy matrix may be formed by the dispersion hardening with the Al$_2$O$_3$ particles in various mass additions and by the precipitation hardening of the matrix. The received results concerning also the enhancement of hardness, even of ca 100% which show the possibility of obtaining the new composite materials with required microstructure influencing the properties the new elaborated composite materials components. Concerning practical implications it can be stated that the tested composite materials can be applied among others in transportation industry but it requires additional research. [1, 2].

The received results show the possibility of obtaining new composite materials with controlled and required microstructure with possible practical implications.

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Characterisation of thermal properties of Cs_2HfCl_6 Crystal by DSC-TG and TMA analyses

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Keywords: Cs_2HfCl_6 single crystal, crystal growth, thermal analysis, DSC-TG, TMA

Recently, cesium hafnium chloride (Cs_2HfCl_6) was discovered as a suitable candidate for application as a cost efficient radiation detector [1]. The Cs_2HfCl_6 is a ternary halide formed by CsCl and $HfCl_4$ mixed together in stoichiometric ratio 2:1 with congruent melting point at temperature 820-826 °C [2, 3]. It crystalizes in a cubic crystallographic structure belonging into a family group of the K_2PtCl_6 structural type materials.

This paper deals with characterization of thermal properties of the Cs_2HfCl_6 crystals. The Cs_2HfCl_6 single crystal was grown from a stoichiometric mixture of CsCl and $HfCl_4$ (2:1) by unseeded vertical Bridgman method in sealed quartz ampoule. The chemical composition of prepared Cs_2HfCl_6 crystals was analyzed using X-ray fluorescence (XRF) and its phase purity using powder X-ray diffraction (XRD). Powder samples ground from selected parts of the crystal (start and end) were used for further analysis. The XRD showed that the content of the Cs_2HfCl_6 phase changed along the ingot: 97 mol% at the start and 22 mol% at the end, respectively. The only secondary phase observed in both samples was CsCl.

The goal of this contribution is to analyze the thermal properties and stability of the Cs_2HfCl_6 under thermal treatment to determine its applications limits. Samples from both parts of the crystal ingot were measured by the non-isothermal simultaneous differential scanning calorimetry and thermogravimetry (DSC-TG) analysis under inert nitrogen atmosphere. The DSC curves of both samples contained effects corresponding to the phase transition of the CsCl from alpha (Pm-3m) to beta phase (Fm-3m) [4, 5]. Further, the eutectic melting temperature of Cs_2HfCl_6 and CsCl phases was detected. Multiple effects observed above eutectic temperature up to 900 °C were ascribed to series of decomposition reactions of the molten solution of CsCl and Cs_2HfCl_6 under release of gaseous $HfCl_4$.

Furthermore, the thermomechanical analysis (TMA) of the orientated Cs_2HfCl_6 platelet (cut and polished from the start of the crystal) was performed to evaluate the Cs_2HfCl_6 coefficient of thermal length expansion. According to the XRD analysis, the platelet was single crystalline with crystallographic orientation [111].

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Characterization of Al_2O_3-Cu-Mo hybrid composite

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Keywords: slip casting, ceramic-metal hybrid composite, DTA/TG analyses, dilatometry test

The present research is focused on the characterization of the composites from Al_2O_3-Cu-Mo system. Hybrid composites are a new group of materials. Their complex phase structure allows obtaining new, better properties not achieved by monolithic materials. The hybrid composites were prepared by slip casting method and subsequent sintering of green bodies in reduced atmosphere. Two series of samples with different volume content of metallic powders were produced in the work: 10 vol.% and 15 vol.% of metal content with respect to the total solid phase content.

The sintering process of the composites was analyzed in detail. The linear shrinkage and the effective coefficient of thermal expansion of composites were measured. The shrinkage curves were obtained by dilatometry test in a heating mode. Composites were characterized by DTA/TG analyses. The phase structure of the samples after sintering was examined by X-ray diffraction. The selected physical parameters were measured by Archimedes method. The microstructure and chemical composition of the Al_2O_3-Cu-Mo materials were analyzed using a scanning electron microscope equipped with an EDS detector. The mechanical properties like a hardness and fracture toughness were measured by Vickers hardness tester.

Dilatometric tests showed that together with the increase in the volume of the metallic phase in the ceramic matrix causes decrease of the starting densification temperature, increase of the temperature where the maximum densification rate occurs, and the decrease of the total shrinkage. The DTA/TG measurements showed the characteristics of the dispersant decomposition to the atmosphere during thermal treatment. The microscopic observations revealed a homogeneous distribution of the metallic phase in the ceramic matrix.

These research were allowed to acquaint the correlation between chemical composition, forming and sintering conditions, and the basic properties of hybrid composites from Al_2O_3-Cu-Mo system.

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Metals, alloys, intermetallics

Thermal analysis techniques applied to determine the continuous cooling curve of DP-590 steel

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Keywords: Dual phase steel, continuous cooling curve, dilatometry, differential thermal analysis

Steel is positioned as the most used material in designing, researching and manufacturing a great variety of products very useful in different industrial sectors, including the automotive industry. In order to not lose its position as strategic material in the international market, the automotive industry develop research projects of new steels grades of ULSAV (Ultra Light Steel Auto Body Vehicle). This concept proposes to replace many conventional steels in vehicles with a new generation of alloys denominated advanced high strength steels (AHSS). Today these new materials bring together a number of important benefits such as low manufacturing cost, ability to reduce the weight of the sheet, improve passenger safety, reduce carbon dioxide emissions to the atmosphere and improve the capacity of recycled than conventional steels. Besides, to optimize shock resistance and fuel economy, the automotive industry is on track to increase the application of Dual-Phase (DP) steels (considered as a AHSS steel grade), in body automotive parts. These steels develop good mechanical properties combination, high strength and drawability aptitude. The key is to achieve an adequate control in the industrial manufacturing process mainly in hot rolling, to generate a biphasic structure of ferrite-martensite or ferrite-bainite. These mechanical properties are achieved through an appropriate kinetic of precipitation and a precisely ratio of specific microconstituents. For this reason it is relevant to revise and increase the knowledge about $\gamma \rightarrow \alpha$ transformation and precipitation at forming process conditions. The characterization and quantification of the different types of ferrite in steels is of great importance in materials engineering. The proportion and distribution of microconstituents strongly influences the steel behaviour [1]. It is well known that other microstructural aspects like the grain size refinement produce increments in strength and toughness [2].

For this reason, the main goal of this paper is to emphasize on the study of the thermal behaviour of a Dual-Phase DP-590 steel in correlation with structural aspects, which justify the mechanical properties. Dilatometry tests integrated with differential thermal analysis (DTA) tests provides useful information of the structural transformations and precipitation phenomena [3]. DP-590 steel samples were tested by dilatometry considering a heating rate of 0.17 °C / s, up to a temperature of 1150 °C and different cooling rates between 0.05 °C / s to 10 °C / s, in air atmosphere. DTA tests were performed in heating and cooling considering two heating and cooling rates (0.05 °C / s and 10 °C / s. The results were correlated with a microstructural study by optical microscopy, scanning electron microscopy (SEM) and Electron Backscatter Diffraction (EBSD) of the samples in order to establish the final proportion of ferrite and bainite achieved at each cooling rate. On this base the continuous cooling curve (CCT) of the steel, was constructed. Applying thermodynamic simulation by Fact Sage 7.2, the phase's transformation temperatures and the precipitation phenomena were corroborated.

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IncRease of thermal diffusivity with heat tReatment in Al-Si-mg alloys

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Keywords: Al-Si-Mg, Thermal diffusivity, Heat treatment, Precipitation, Si segregation

Al-Si-Mg alloys such as A6061 (Al-0.2Si-0.4Mg) are widely used as materials for producing heat sinks due to their low density, high strength, and high thermal conductivity. Thermal conductivity is one of the most essential characteristics in the heat dissipation of the heat sink, and it is critical to know the change in the thermal conductivity characteristics depending on the microstructure. It is generally well known that the spheroidization of eutectic Si improves the thermal conductivity, however, few studies have been carried out on the effects of the secondary phase and the eutectic phase distribution. In this paper, the effect of the microstructure change (secondary phase and eutectic phase distribution) on the thermal conductivity of Al-Mg-Si alloys was investigated. The two types (Al0.2Si0.4Mg and Al6.5Si0.4Mg) of Al-Si-Mg alloys used in this study were prepared by atmospheric gravity casting. The heat treatment of the Al0.2Si0.4Mg used for the thermal analysis was conducted by solid solution heat treatment at 535 °C for 5 hours and then quenched in the warm water of 80 °C. The solid solution heat treatment of Al6.5Si0.4Mg was carried out at the same temperature with 10 hours. Artificial aging of specimens was performed in air at different temperatures of 180, 200 and 240 °C for 5 hours. After aging treatment, the changes of microstructure due to the heat treatment was examined using **optical microscopy** (OM), differential scanning calorimeter (DSC) and transmission electron microscopy (TEM). The variations of thermal diffusivity according to microstructure were investigated by using a laser flash apparatus (LFA). Three types of phases were formed during the casting process: eutectic Si, Al-Fe-Si intermetallic compound and Mg_2Si phase. The fiber-like eutectic Si of Al6.5Si0.4Mg was found discontinuously distributing in Al matrix after solid solution treatment. The thermal diffusivity of Al6.5Si0.4Mg alloys increased with the increase of solid solution treatment time due to the spheroidization of eutectic Si. In all samples, the precipitation of Mg_2Si and Si phase increased thermal diffusivity after aging treatment.

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Investigation on interface formation and linear thermal expansion of Fe/Al bimetal by high pressure die cast bonding

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Keywords: interface formation, linear thermal expansion, bimetal, cast bonding, die-casting

Fe/Al bimetals have been widely applied in various vehicle parts which performed on thermal fatigue environment because of their high specific strength [1, 2]. Bimetal products consisted of two alloys are manufactured in several ways such as roll bonding, extrusion coating, and casting bonding. Among the above of mentioned methods, cast bonding by high pressure die casting is a unique process with good metallurgical bonding, low cost, and high efficiency because of high injection speed and pressure. Cast bonding by high pressure die cast is a method of casting molten aluminum onto the solid cast iron surface and bonding it by thermal diffusion. During the cast bonding process, intermetallic compounds are formed at the interface between the two alloys by atomic diffusion. The intermetallic compound thus formed can affect the thermal expansion characteristics of the bimetal parts.

In this study, the interfacial formation and linear thermal expansion of Fe/Al bimetal by high pressure die cast bonding were investigated. Particularly, in order to apply Fe/Al bimetal to automobile parts, it is very important to study the effect of the interfacial compound formed by cast bonding on the linear thermal expansion. The high-pressure die casting process was controlled with several parameters such as injection speed, hold time and pressure. The composition and the intermetallic compound layers were observed using an optical microscope, a scanning electron microscope, and an electron probe microanalysis. Linear thermal expansion of each specimen was measured using a thermo-mechanical apparatus (TMA, Netzsch Inc. TMA 405 F3). Specimens for the dilatometric test were prepared with a diameter of 12.7mm and a height of 25 mm. TMA analysis carried out from room temperature to 300 ºC with a heating rate of 10 K/min in purified N_2 gas of a flow rate of 50 ml/min.

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Effect of intermetallic compound layer on thermal diffusivity of cast-bonded Al-CU bimetal

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Keywords: Bimetal bonding, Cast bond, Intermetallic compound, Thermal diffusion, Aluminum, Copper

Recently, bimetallic bonding has been actively studied to make up for the disadvantages of the two materials and to take advantage of them. [1,2]. Copper has excellent strength, ductility, and processability, and it has very high heat and electric conductivity. However, it is combined with other materials such as aluminum to compensate for the heavy and costly disadvantages of copper. Bimetal bonding can reduce the conductivity, which is an advantage of copper, but aluminum is suitable as a bimetal bonding material since it is a conductive metal next to copper except for precious metals. Brazing is widely used for Al-Cu bimetal bonding, but the process is complicated, the process cost is high, and there is a problem that the conductivity is lowered because the filler is included between Al-Cu. Therefore, the bimetal bonding of Al-Cu has been studied using a casting method that is simpler and cheaper than the brazing.

The thermal conductivity can be influenced by the intermetallic compound layer formed by thermal diffusion during the casting bonding. In this study, the effect of the thickness change of the intermetallic compound layer on the thermal diffusivity according to the annealing time was investigated by heat treating the intermetallic compound layer formed in the Al-Cu cast bonding. All sides Cu specimen were polished to # 600 and located on a center of a graphite mold with a width of 100 mm, a length of 150 mm and a height of 22 mm. Pure aluminum (99.9%) melted at 720 °C was poured into a graphite mold to make Al cast bonding to the surface of Cu and then air-cooled in the atmosphere. The heat treatment was carried out at 400 °C for 15, 30, 60, 130, 240 minutes. The cast bonded specimens were cut to a thickness of 4 mm, and the composition and thickness of the intermetallic compound layer formed on the interface of bimetal were observed using an optical microscope, a scanning electron microscope, and an electron probe microanalysis. Intermetallic compounds with Al_2Cu, AlCu, and AlCu were found at the Al-Cu bonding interface. The thickness of each compound layer increased with increasing the heat treatment time. The thermal diffusivity according to the intermetallic compound layer was measured using a laser flash apparatus (LFA).

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DTA/DSC measurements in Ag-Au-Ga system

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Keywords: Ag-Au-Ga system, DTA measurements, liquidus line

In recent years, an interest in the use of gallium and its compounds has increased. The introduction of gallium into multi-component alloys should bring down their melting temperature. This effect can be used in the amalgam bonding process [1]. Gallium has also found application as a component in shape memory alloys which exhibit a magneto-mechanical effect [2,3] as well as in CIGS and jewelry materials [4,5]. The ternary Ag-Au-Ga system can be applied in electronic and jewelry industries. Information on the course of the liquidus line in this metallic system can be obtained by applying differential thermal analysis, DTA. The ternary Ag-Au-Ga system was investigated along the following cross-sections: X(Ag)/X(Ga)=1:1 and X(Au)/X(Ga)=1:1. DTA analysis were carried out in heating and cooling cycles with three rates: 1, 5 and 10 K/min. Next, the course of the liquidus line in the Ag-Au-Ga was determined. Additionally, other thermal effects were derived from heating curves. The obtained results are compared with the results of calculations of the Ag-Au-Ga system in which existing information only from respective binary systems have been used.

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Effect of precipitation on the thermal properties of Aluminum-silicon foundry alloy

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Keywords: aluminum alloy, thermal diffusivity, thermal expansion, precipitation, artificial aging treatment

Al-Si alloy systems are most commonly used as aluminum casting alloys because of their excellent fluidity and castability. In particular, Al-Si-Mg-Cu is widely used in automotive engine applications such as engine blocks, cylinder heads and pistons [1–3]. In a mass production environment, repetitive use of mold increases mold temperature and affects the cooling rate of the product. Changes in the cooling rate affect the microstructure of the silicon particles in the Al-Si alloy and thus change the physical properties of the product. In order to improve the physical properties of the alloy, it is necessary to control the size and shape of the microstructure. The relationship between physical properties and microstructural changes have been studied according to the cooling rate during the solidification process. However, previous studies have focused only on improving mechanical properties, and few studies have investigated the changes in thermal properties due to microstructures. Therefore, the purpose of this study is to examine the effect of heat treatment on the thermal property of Al-Si-Mg-Cu alloys with different mold temperatures.

The material used in this study was Al-9Si-0.4Mg alloy supplied by Altechno Metal Inc. Copper was added to the melt from pure Cu (99.9 wt.%). Melting was carried out in a 30 kg capacity SiC crucible using an electrical resistance furnace. The melting temperature was held at 730 °C. The melt was degassed at 740 °C for 15 minutes using Ar gas bubbling. The melt was then further held for 20 minutes before pouring into a steel mold. The molds were preheated to two different temperatures to evaluate the effect of varying mold temperature on the thermal properties. The molds were preheated to the temperature of 95 °C (M95) and 200 °C (M200), respectively. All preheated mold temperatures and heat treatments in this study were based on the mass production conditions of the cylinder head in a motor company of Korea. The heat treatment of the specimens used for the thermal analysis was conducted by solid solution heat treatment at 535 °C for 6 hours and then quenched in the warm water of 80 °C. The artificial aging of the specimens was carried out in the air at 180 °C for 5 hours, respectively. After aging treatment, the specimens were cooled naturally at room temperature.

The changes of thermal properties according to microstructure were investigated by using thermal diffusivity, the coefficient of thermal expansion and differential scanning calorimetry (DSC) analysis. Thermal diffusivity was measured using the laser flash technique. Specimen for the thermal diffusivity was prepared from the casting to a diameter 12.7 mm and a thickness of 2.5 mm. Solid state phase changes were studied by dilatometry. Dilatometric tests were performed using a thermomechanical analyzer with a resolution of 0.125 nm. Specimens for the dilatometric analysis were prepared from the casting with a diameter of 6 mm and a height of 25 mm. The surface was polished longitudinally up to 2400 grit to remove the machining notch effect. The DSC was measured using a differential scanning calorimeter with synthetic sapphire as the reference material.

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Structure, properties and phase transformation of CuNi2Si alloyed copper

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Keywords: alloyed copper, thermal analysis, depth sensing indentation, corrosion resistance

The work presents the structure and corrosion resistance of alloyed copper CuNi2Si. The most common are three types of this copper alloy grade with a nickel concentration of 1.3; 2.0 and 3.5% and silicon with a concentration of 0.5 to 1.2%. In the majority of alloyed copper, heat treatment is used, which involves supersaturation and aging, which plays a key role in forming both mechanical and physical properties.

The alloy was subjected to classical treatment: supersaturation in water after annealing at 950°C for one hour and then aging at 600°C for 1, 2, 4 and 7 hours. The structure of the CuNi2Si1 alloyed copper were analyzed by high resolution transmission electron microscopy (HRTEM). As a result of studies of corrosion resistance of the anodic polarization curves were obtained for all four treatment options. It was investigated further course of phase transformations occurring in the melt by means of differential scanning calorimetry. The elaborated research results present some utilitarian qualities since they can be used in development of process conditions for industrial scale production of strips from CuNi2Si alloy of defined properties and operating qualities.

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Thermal analysis of Ag-Ni-Cr alloy for transportation usage after fibre laser alloying

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Keywords: Surface treatment; Differential Scanning Calorimetry, Fibre laser, Silver alloys; Laser feeding, Metal powder

The most effective way to design, produce, analyse and optimize new and existing industrial thermal processes of metal treatment, including laser based techniques, is to develop a quantitative knowledge and understanding of the thermal relationships occurred between temperature and timed, which allow the desired forming of properties of the final products. The purpose of this paper is the application and evaluation of DSC analysis used for silver-nickel-chromium alloy. The obtained DSC curves from heating and cooling run allow to identify the peak transitions temperatures of the obtained phases present after laser surface treatment and the fibre laser line energy influence on the microstructure and properties of the surface layer. The goal of this work was also to investigate the influence of fibre laser beam as well as determine technological conditions for the laser alloying process of the surface layer as well as microstructure and properties changes occurred in the obtained surface layer of silver (Ag), to make clear an effect of nickel (Ni) and chromium (Cr) metal powder addition on structure and properties of the laser remelted metal surface, like wear resistance and hardness. Historically, to increase hardness, copper was added to silver and the way in which this affects the annealed hardness of the resulting silver-copper alloys is that the traditional sterling silver composition of 92.5% silver 7.5% copper, the hardness values published by the major manufacturers for the fully annealed condition are 75 HV. Based on the performed investigations it was possible to obtain a layer consisting of the heat affected zone, transition zone and remelted zone, with higher hardness value compared to the non remelted material. A powder size alloying was chosen, according to the available power, ensuring a proper remelting and alloying process. As a result of alloying of the Ag alloy with metal powder the surface layer can be enriched with the metal particle and in some cases a high-quality top layer is possible to obtain. Concerning original practical implications of this work it was important to investigate the appliance possibility of Fibre Laser for enhancement of the surface properties. The scientific reason was also to describe structure changes and compounds occurred in the laser remelted surface silver layer after Ni and Cr particle feeding into the material. It is possible to extend the appliance and development of modern technologies in

the field of surface material engineering can be extended by laser surface treatment, using fibre laser for alloying and remelting. The main goal of this work was to investigate the microstructure of the laser treated Ag alloys as well as the add metal powder particle distribution in the surface layer of the alloyed and remelted material. Important is also the determination of the laser treatment parameters, particularly the laser power, to achieve a high value of layer hardness for protection of the new develop material from losing their properties and to make the tool surface more resistant. The purpose of this work was also to determine technological and technical conditions for feeding into the surface layer with fibre laser. The achieved results of new laser treatment method used for metal surface treatment are presented and discussed, where special attention was devoted to monitoring of the layer morphology of the investigated material, as well as the structure investigation of the obtained surface layer allowing it to achieve a high layer hardness. Optical and electron microscopy (SEM) were used to characterize the microstructure of the obtained surface zones, the possible addition metal distribution and intermetallic phases created after laser beam energy influence in the surface area. The investigation helps to use this technique for alloying of transition metal alloys. The scientific goal of this work is the usage of fibre laser for improvement of mechanical properties, especially the surface hardness. It was found that, the obtained surface layer is in case of chromium application without cracks and defects as well as has a relatively higher hardness compared to the non-treated material. Also the distribution of the fed metal is good, but there are still possibilities for further modelling. The hardness value increases in general according to the laser power used so that the highest power applied gives to highest hardness value in the treated surface. The major purpose of this work is to study the effect of a fibre laser on silver chromium structure to provide application possibilities for transportation industry.

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Thermodynamic behavior of some 3D, 4D and 5D aluminides: The case of Al-V, Al-Ru and Al-Re systems

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Keywords: phase diagram, CHALPHAD, Aluminium, thermodynamic properties

For high-temperature materials, as Ni-based and Fe-based super-alloys, intermetallic compounds containing aluminum and transition metals (Ni, Ti, Zr, Hf, V, Nb, Ta) have drawn a considerable attention as a candidate material qualified for high-temperature applications in aggressive environment. Because of its unusual high melting point, high strength, in addition to the oxidation and corrosion resistance properties and good thermodynamically stable [1, 2], Al-V, Al-Ru and Al-Re based compounds are promising high-temperature materials. Importantly, the high-temperature applications of these materials are also markedly influenced by the structural stability and thermodynamic properties. Therefore, phase equilibria and thermodynamic quantities must be well determined.

It should be noted that the Al-TM (TM=V, Ru and Re) phase diagrams have not been fully characterized because of many experimental difficulties. The most restrictive one is the very large difference between the melting points of the starting elements: 660 °C for Al, and 3186 °C for Re. However, there is a lack of the systematical calculations of the phase stability and thermodynamic quantities as well as elastic properties and electronic structures for the intermetallic compounds.

The aim of this work is to compile all the available experimental information, to confirm their consistency and to create an optimized set of thermodynamic data by means of the CALPHAD (CALculation of PHAse Diagram) approach. In this context and based on the recent experimental information concerning the Al-rich part of the Al-Ru and Al-Re phase diagrams [3, 4], we have assessed these binary systems. The Redlich–Kister polynomials as well as the exponential temperature dependence model of Kaptay were used to describe the excess Gibbs energy of all occurring phases.

In this work we presents a systematic study of the evolution of the thermodynamic properties of the 3d, 4d and 5d TM-aluminide intermetallics, depending on the location of the TM element in its relative series.

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Modification of eutectic Mg2Si phase in AlMg5Si2Mn alloy by Sr addition

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Keywords: aluminium alloys, foundry, modification, thermal analysis, Sr addition

Aluminium foundry alloys are widely used as structural materials in automotive, aerospace and other industries because of their high strength to weight ratio. The most used Al casting alloys contain high silicon content, in the range 3-15 wt.%, which improves the castability and reduces the material's thermal expansion coefficient. Silicon precipitates from liquid in the form of coarse brittle compounds or brittle platelets during the Al + Si eutectic reaction [1], which reduce the workability and ductility of the alloy. During the last years, Al foundries have shown increasing interests in Al-Mg-Si-Mn casting alloys which are considered as potential competitors for established Al-Si based alloys [2]. However, the ductility and mechanical properties of these alloys are strictly influenced by the amount, distribution, size, and morphological characteristics of the eutectic Mg_2Si phase. Brittle and interconnected eutectic Mg_2Si particles are commonly observed in the microstructure; they provide favourable initiation sites and easy path for crack propagation [3]. The purpose of this work is to evaluate the use of thermal analysis to explore the solidification kinetics of a modified AlMg5Si2Mn alloy. Metallographic and thermal analysis techniques [4] have been used to quantitatively examine the microstructural changes occurring with Sr modifier additions. The cooling curves and the corresponding derivative curves were plotted to determine the nucleation temperature, minimum, and growth temperatures for Al-Mg_2Si eutectic reaction, based on the first derivative cooling curve approach [4]. The results indicate how the presence of Sr in AlMg5Si2Mn alloy promotes nucleation of the eutectic Mg_2Si particles at lower undercooling and interact during their growth phase (Fig. 1). The eutectic Mg_2Si phase in unmodified AlMg5Si2Mn base alloy tends to show coarse script-like morphology, which transforms into refined fibrous structure with the addition of Sr.

Illustrations

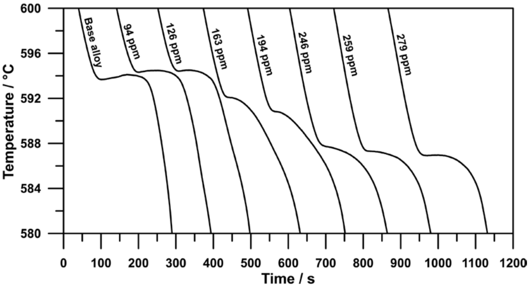

Fig. 1. Cooling curves, with focus on the eutectic reaction, for all tested Sr levels in AlMg5Si2Mn alloy.

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Study of high-temperature mechanical properties and thermal diffusivity of H13-deposited material fabricated through DED Process

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Keywords: Laser Deposition, Thermal Diffusivity H13, High-temperature Mechanical Properties

The Direct Energy Deposition (DED) method using a laser is a 3D metal printing technique that melts a metal surface by using a high-energy laser and simultaneously deposits a metal powder by injecting and melting it. Particularly, in recent years, studies have been conducted to apply the DED process to products such as die casting molds exposed to high-temperature and high-pressure in order to improve their high-temperature durability.

This study performed the comparative evaluation of high-temperature durability for the following: a specimen fabricated through the DED process using H13 metal powder, a high-pressure casting mold material, and a specimen of heat-treated bulk H13 material.

To compare the high-temperature durability between the two specimens, the deposited specimens were fabricated for conducting the high-temperature Vickers hardness measurement test, the high-temperature shear test, and the thermal diffusivity measurement test. Using the fabricated specimens, each test was carried out at four stages of temperatures from room temperature (25 °C) to a maximum of 800 °C.

From the results of high-temperature hardness test, the heat-treated H13 material and the deposited H13 material showed that the hardness decreased as the temperature increased and sharply decreased from 600 °C and above. In the high-temperature shear test conducted to measure interface adhesion at high temperatures, the test load decreased as the temperature increased, whereas the displacement showed an increasing trend. Moreover, in every temperature section, no interfacial cutting occurred. The thermal diffusivity at 25 °C of the heat-treated H13 specimen and the DED-deposited H13 material was 6.406 mm^2/s and 5.103 mm^2/s, respectively. For the thermal diffusivity test, the high temperature of these specimens decreased slowly up to 700 °C and then increased slightly at 800 °C.

Nanofluids

Study of synthesis, stability and thermal properties of carbon sphere based nanofluids

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Keywords: nanofluid, carbon sphere, stability, synthesis

In the present study, carbon nanosphere was prepared using hydrothermal method at 180 oC with sucrose solution and NaOH solution as starting materials. Carbon nanosphere – distilled water nanofluids were prepared with concentration between 0.001 and 0.1vol% without any surfactants. The synthesized nanoparticles were characterized by X-Ray differeaction (XRD), Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Stability of the nanofluid was investigated by Zeta potential and UV-VIS spectroscopy. Thermal conductivity of the nanofluid was higher than the base fluid. From the zeta potential test, the nanofluids were considered to be stable.

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Investigation of thermal conductivity, viscosity, and zeta potential of tungsten trioxide based nanofluids

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Keywords: nanofluid, tungsten oxide, stability, preparation

Stable and well dispersed hexagonal tungsten oxide (h-WO_3) – distilled water nanofluids having h-WO_3 volume concentration between 0.001 and 0.01vol% were prepared without any surfactants. 50-70 nm h-WO_3 nanoparticles were prepared by controlled annealing of hexagonal ammonium tungsten bronze, $(NH_4)_xWO_{3-y}$ in air at 470 °C. For the preparation of 5-10 nm thick and several micrometer long h-WO3 nanowires, microwave assisted hydrothermal synthesis method was applied at 160 °C with Na_2WO_4, HCl and $(NH_4)_2SO_4$ as starting materials. The h-WO_3 nanoparticles are characterized using XRD, SEM, and FTIR spectroscopy. Thermal conductivity, zeta potential and viscosity measurements are performed as a function of h-WO_3 loading at room temperature. The zeta potential test indicates that the nanofluids are stable. The thermal conductivity of the nanofluid was higher than the base fluid.

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I. M. Szilágyi thanks for a János Bolyai Research Fellowship of the Hungarian Academy of Sciences. The ÚNKP-18-4-BME-238 New National Excellence Program of the Ministry of Human Capacities, Hungary. A GINOP-2.2.1-15-2017-00084, an NRDI K 124212 and an NRDI TNN_16 123631 grants are acknowledged. The work performed within project VEKOP-2.3.2-16-2017-00013 was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund. The research reported in this paper was supported by the Higher Education Excellence Program of the Ministry of Human Capacities in the frame of Nanotechnology and Materials Science research area of Budapest University of Technology (BME FIKP-NAT).

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Analysing the behaviour of copper oxide-thermal oil on forced convection and pressre drop in upward and downward flow in plain and microfin tube

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Keywords: nanofluid, forced convection, downward, upward flow

The effects of using copper oxide-thermal oil on convective heat transfer and pressure drop in a downward flow in an inclined microfin tube is investigated experimentally in this research. The flow regime and wall temperature are laminar and constant, respectively. The effects of nanofluid, Graetz number, Prandtl number, negative and positive inclination angles, on convective heat transfer augment moderately with the surge in nanoparticles mass concentration. Correlations are advisable to anticipate Nusselt number and Darcy friction factor in upward and downward single-phase flow in microfin tube under constant wall temperature and laminar flow in inclined plain and finned tubes. The maximum aberration is lower than 21% which is admissible to predict experimental data. Accompaniment of heat ration with pumping power ration is presented in this paper. If the increment of pressure drop is more than heat transfer enhancement, it will not be appropriate to use CuO-thermal oil, negative inclination angles and microfin tube. The maximum FOM is 64% which is calculated with 1.5% nanoparticles mass concentration and inclination angle 60º at Prandtl number 349 in microfin tube.

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Rheological and thermodynamic behavior of gemini /UMP hydrogel systems and their interaction with α-Chymotrypsin enzyme

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Keywords: gemini surfactants, hydrogel, rheological behavior, thermodynamics, DSC

In recent years, hydrogel systems have attracted considerable attention due to their theoretical significance and potential industrial applications in many areas[1,2]. Surfactant hydrogel can be formed by self-assembling of amphiphilic molecules through non-covalent interactions, including hydrogen bonds, π-π stacking, electrostatic interactions, van der Waals forces, and synergistic effects[3]. We have prepared the hydrogel with mixtures of a cationic gemini surfactant $C_{14}C_2C_{14}Br_2$ and 5'-Uridylic acid (UMP) in aqueous solution. In this work, the rheological properties of aqueous solutions of $C_{14}C_2C_{14}Br_2$/UMP and their thermodynamic behaviours were studied by steady and dynamic shear rheometry, differential scanning calorimetry (DSC) and Cryo-TEM. Thus both the microstructural characteristics and phase transition temperatures of the hydrogel system were analyzed in detail. All the studied solutions with different mole ratios of $C_{14}C_2C_{14}Br_2$/UMP show shear-thinning behavior and exhibit a typical viscoelastic response. The viscoelasticity of the solutions may be attributed to the presence of wormlike micelles, which leads to the formation of a three-dimensional network by their entanglement. The phase transition temperature ($T_{\text{gel-sol}}$) of the hydrogel systems was obtained by DSC. The results show that the phase transition temperature of the gel systems increases as the concentration of the system increases, which means the gel structure becoming more stable. When *α*-chymotrypsin (*α*-CT) was added into the gel system the critical shear rate increases with the increase of concentration of the *α*-CT. These results lay a foundation for further exploring the mechanism of gel formation, the stimuli response of gel and the basic physicochemical properties.

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Pool boiling of nanofluid using heat flux partitioning model: CFD investigation

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Keywords: Nucleate boiling, HFP model, wettability, Fluent 18.2 and nanofluids

In the present work, a new simulation of nanofluid/ vapor two-phase flow inside the 2-D rectangular boiling chamber achieved. The Eulerian-Eulerian approach was used to mimic the boiling curve and the interaction between the phases. The modification on the boiling parameters such as surface roughness and enhancement of wettability that represented by reducing the contact angle between the solid surface and liquids during boiling of nanofluids takes in our account in this study. New closure correlations regard the density of the nucleation sites and bubble departure diameter as well as the bubble waiting time coefficient under quenching model correction were included to improve the results of this simulation. The validation of numerical results with those obtained from experimental works revealed good agreements for both pure water and nanofluids. The results found that when improving the classical heat flux partitioning model HFP [1, 2] by considering the modification of nucleate boiling parameters, it will give a good agreement with experimental data and more mechanistic sights to those of well known correlation that available in literature such Rohsenow correlation and even for classical HFP model itself when using boiling of nanofluids.

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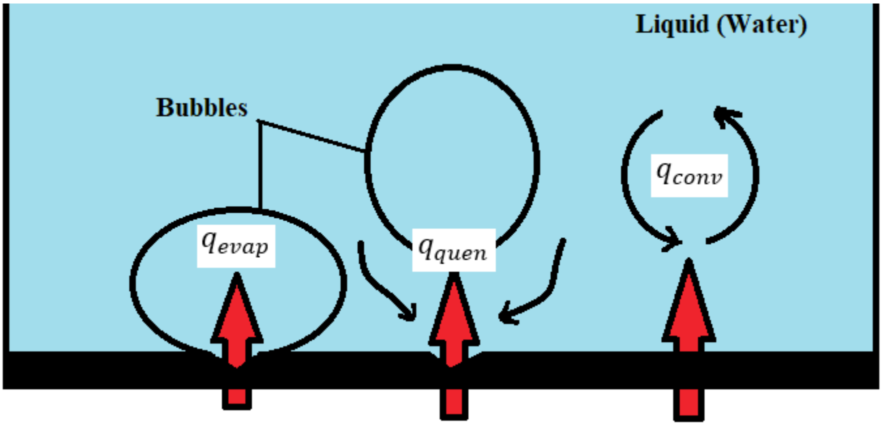

$$q_{total} = q_{conv} + q_{evap} + q_{quen}$$

Fig. Mechanism of heat flux partitioning boiling model.

MHD combined convection of Non Newtonian nanofluid in an inclined lid-driven cavity containing a hot obstacle

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Keywords: Mixed convection, Nanofluid, Magnetic field, inclined square cavity.

In this study, under the influence of the magnetic field the mixed convection of Non Newtonian nanofluid in a lid-driven cavity containing a hot obstacle was studied numerically. The right and left walls are cold, the top wall is adiabatic, and the bottom wall is hot. The governing equations are solved using finite volume formulation and the SIMPLER algorithm is used for pressure–velocity coupling. The problem was simulated at different Richardson number $0 \leq Ri \leq 10$, Reynolds number $50 \leq Re \leq 500$, Hartmann number $0 \leq Ha \leq 100$, inclination angle $0 \leq \alpha \leq 135°$ and solid volume fraction $0\% \leq \varphi \leq 5\%$ with Prandtl number $Pr = 7$. Based on the cooling optimization of cold walls, the obtained results show that by Increase in Richardson number in a constant volume fraction and cavity angle decreases the Nusselt number. In addition, the presence of a magnetic field is manifested by the decrease of the velocity intensity and consequently, the mitigation of the flow structure.

Nanomaterials and composites

Synthesis and Catalytic Activity Studies of α-MNO_2 Nanorods, Rutile and Its Composites Prepared by Hydrothermal Method

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Keywords: Alpha MnO_2, titanium dioxide, Thermal Gravimetric, nanoparticles

Alpha MnO_2 exhibits an excellent catalytic activity in different chemical reactions, functions as enzyme alternative, as so-called artificial enzyme which is used in different applications such as industrial, environmental and biological applications (antibacterial activity). In this work, alpha manganese dioxide (α-MnO_2) and titanium dioxide/rutile (TiO_2) nanostructures have been synthesized by hydrothermal method (autoclave) from potassium permanganate ($KMnO_4$) and titanium tetrachloride ($TiCl_4$) as precursors. α-MnO_2 was annealed at different temperatures (250–700˚C). The structure and surface morphology of these nanostructures and its composites were characterized by X-ray diffraction (XRD) which showed the presence of α-MnO_2 particles. Atomic Force Microscope (AFM) investigations showed the average grain size is around 66.27–81.65 nm. Field Emission Scanning Electron Microscopy (FE-SEM) studies revealed that the α-MnO_2 nanoparticles composed of uniform nanorods and bundle of nanorods with average outer diameter of 42–53 nm having different lengths. Thermal Gravimetric studies (TG) have confirmed the high purity of the prepared nanoparticles and decomposition steps of MnO_2. Fourier Transform Infrared Spectrometer FT-IR measurements proved information on vibrations of functional groups in the metal oxide, UV/Visible technique shows the energy gap (Fermi level) of MnO_2 at different annealing temperatures. The catalytic activity of α-MnO_2 was studied by using a novel colorimetric method by measuring the decrease in color density resulted by acidic solution of potassium permanganate or manganese dioxide nanoparticles with hydrogen peroxide in room temperature for 3 minutes at wave length of 525 nm and it was found that the maximum activity of α-MnO_2 nanopowder was achieved after pretreatment/annealing at 400 ˚C. There was a decrease in the catalytic activity of MnO_2-TiO_2 composite (ratio of 3:1) annealed at 400 ˚C in the decomposition reaction of H_2O_2 as compared to that of pure α-MnO_2 nanopowder. This may be due to the change (distortion) in structures of α-MnO_2 and TiO_2 nanoparticles which results in decrease in the activity.

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Influence of temperature and bn nanoparticles on UV, thermal and dark curing of a cycloaliphatic epoxy resin

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Keywords: cycloaliphatic epoxy, BN nanoparticles, UV-curing, dark curing

In this work the influence of boron nitride (BN) nanoparticles on the kinetics of cationic photopolymerization and thermal polymerization of an epoxy system was investigated employing DSC, photo-DSC and FTIR spectroscopy. Previous investigations have reported that the addition of BN micro-particles allowed increasing thermal conductivity of thermally cured epoxy thermosets [1]. A difunctional UV-curable cycloaliphatic epoxy resin (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate) was used as precursor of the polymer matrix. The resin was photopolymerized in the presence of triarylsulfonium hexafluoroantimoniate salts (cationic photoinitiator). Different amounts of photoiniciator were used (2–3%). The BN/epoxy dispersions containing 4.6 wt% of BN in the epoxy resin were obtained by sonication.

The epoxy conversion during UV irradiation was determined at seven temperatures, from 30ºC to 90ºC in the photo-DSC. The photo DSC did not register exothermal heat flow after 6 min of UV irradiation in the epoxy resin neither in the BN/epoxy dispersions. The conversion reached was strongly dependent on temperature in accordance with results reported for a similar photo-curable epoxy system [2].Moreover conversion is influenced by BN presence. Lower photocuring rates and lower conversion degrees were obtained for BN/epoxy dispersions.The photo-polymerization kinetics was analysed using an autocatalytic model.

After the UV curing, the samples were subject of thermal dynamic curing in the DSC, as expected the higher the conversion in photo-curing, the lower the conversion in dynamic curing, reaching a total conversion 60–70%. The thermal curing was less affected by the presence of BN than UV curing.

UV irradiated samples for 7 min at 40ºC were kept under isothermal dark-curing (40ºC) up to one month giving rise to significant conversion increases, reaching ~70% in neat epoxy but BN /epoxy nanocomposites only reached ~60% conversion. Thermo-mechanical measurements of dark cured samples evidence a heterogeneous epoxy matrix, thermal postcuring eliminates the matrix heterogeneity. The Tg of the epoxy matrix is significantly reduced in the presence of BN nanoparticles.

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Thermal properties and non-isothermal crystallization kinetics of biocomposites based on polylactide, rice husks, and cellulose fibres

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Keywords: biocomposites, poly (lactic acid), cellulose, rice husks, surface treatment

Bioplastics reinforced by agricultural waste fibers show promise to provide degradation back into the environment when they are no longer needed. These biocomposites have the potential to replace synthetic polymers from non-renewable resources in some applications and may turn out to be one of the material revolutions of this century. Unlike synthetic composites, biocomposites are renewable, carbon neutral, biodegradable, non-petroleum based, and have low environmental, human health and safety risks. In this paper, poly (lactic acid) (PLA) based biocomposites filled with cellulose fibers (CF) and rice husks (RH) at 10 wt. % loading were prepared by twin screw extrusion and injection moulding. Particular attention was given to the enhancement of adhesion between the polymer matrix and natural filler through the acetylation (A), ozone (O) and dielectric barrier discharge (DBD) plasma (P) surface treatments. The non-isothermal crystallization behavior and thermal properties were investigated through Differential Scanning Calorimetry (DSC) under various cooling rates (5, 10, 20 and 40 °C/min). Morphology and filler/matrix adhesion was investigated through Scanning Electron Microscopy (SEM). The addition of both fillers increased overall crystallization kinetics of resulted biocomposites, especially at lower cooling rates. An increase in crystallinity degree from 4.3 % (neat PLA) to 64 % has been observed for PLA/CF-P samples at 5 °C/min cooling rate. The Heat Deflection Temperature (HDT) measurements were conducted to investigate enhancements in thermal stability of resulted biocomposites.

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Termomechanical properties, morphology and non-isothermal crystallization of solid and microcellular biocomposites based on stereocomplexed polylactide and cellulose nanocrystals

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Keywords: biocomposites, microcellular injection molding, cellulose nanocrystals, poly (lactic acid), stereocomplex

Poly(lactic acid) (PLA), a leading biobased, biodegradable and biocompatible thermoplastic still faces some drawbacks related to slow crystallization rate, low impact resistance and heat deflection temperature. Herein, is this problem addressed by the stereocomplex formation between PLA that is mainly composed of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) at 5 wt. % loading by melt-blending. The addition of a small amount of PDLA nucleation agent aims to create a high melting point stereocomplex phase. Furthermore, second heterogeneous nucleation agent (5.5 wt. %) based on cellulose nanocrystals (CNC) with an interface compatibilizer composed of maleic anhydride (MAH) grafted PDLA was prepared. Melt-blending of PDLA-g-MAH/CNC masterbatch was conducted through reactive extrusion with dicumyl peroxide (DCP) as a radical initiator. Both solid (s) and microcellular (m) samples were prepared by injection molding technology. Nitrogen (N2) physical blowing agent in a supercritical state was used to prepare lightweight samples. The effect of nucleation on the crystallization, morphology and thermomechanical properties of both solid and microcellular samples is investigated. The non-isothermal crystallization behavior was investigated through Differential Scanning Calorimetry (DSC) under various cooling rates (2.5, 5, 10 and 20 °C/min). Morphology was investigated through Scanning Electron Microscopy (SEM) and infrared spectrum of absorptions were analysed through Fourier-Transform Infrared (FT-IR) spectroscopy. The Dynamic Mechanical Analysis (DMA) and Heat Deflection Temperature (HDT) measurements were conducted to investigate enhancements in thermomechanical properties. The increase of nucleation density and specific stereocomplex interaction at interphase of PLA/PDLA blends and PLA/PDLA-g-MAH/CNC nanocomposites results in improvement of crystallinity, storage modulus and heat deflection resistance.

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Investigations on the thermal conductivity of aerogel insulation blankets - hygrothermal analysis

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Keywords: thermal conductivity, permeability, absorption, partial immersion, total immersion

The European Union's 2050 long term strategy is that of a decarbonized economy that will ensure a better and longer life for our planet. The 2050 Energy Strategy implies that about 80–95% greenhouse gas emissions must decrease by 2050 with 80 to 95%, when compared to pre-industrial levels. In the building industry, important participants at the long term strategy are the construction materials. Thereby, the paper presents investigations done on the aerogel blanket, a nano insulation material used in the building industry, in the past years. The aerogel blanket has superior thermal insulating properties at reduced thickness, due to its thermal conductivity, which is lower than that of common thermal insulations. The material thermal conductivity is measured with both a laboratory heat flow meter and also with a field instrument equipped with heat flows and temperature sensors. The determinations are done on samples exposed to different temperature and humidity conditions in order to observe their influence on the aerogel thermal conductivity. At the same time, there are measured the short term and long term water absorption capacity of the material through partial and total immersion. Other samples are kept in total immersion in water until they reach saturation phase. On the respective samples are determined: the water absorption capacity in order to reach saturation, the hygric expansion and the thermal conductivity after being dried to a constant mass. The results indicate that the exterior humidity and the material water content are important factors which influence the aerogel thermal conductivity.

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Impact of nanocrystalline cellulose on the properties of LLDPE

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Keywords: nanocrystalline cellulose, linear low density polyethylene, maleic anhydride polyethylene, high energy ball milling

Nanocrystalline cellulose (CNC) has emerged as an attractive filler for polymers, due to its high stiffness, low toxicity, low cost and its renewable nature [1]. As a result, over the last years, a significant amount of research has been dedicated to the investigation of its reinforcing effect on a series of polymeric matrices [2]. A major part of those studies is performed through wet processing methods, though this approach is both time consuming and hardly implemented in the industrial scale. On the contrary, little research has been carried out in CNC nanocomposites manufactured by the melt processing technique, since it can cause CNC breakage, failure of matrix-filler interaction and poor filler dispersion, leading to poor mechanical performance of the respective nanocomposites [3].

Thus, the goal of this study is the achievement of a fine dispersion of CNC in linear low density polyethylene (LLDPE) without employing wet methods, but with the melt mixing technique. The procedures followed in current study in order to achieve improved compatibility at the CNC – matrix interface and to enhance the degree of dispersion of CNC within LLDPE are the use of maleic anhydride polyethylene (PE-g-MA) as a coupling agent and the physical premixing procedure with solid state high energy ball milling. The nanocellulose content was set between 0.5 and 2.5 wt%, while a thorough study was performed to the nanocomposites in terms of their structural, thermal and mechanical properties. More specifically, Fourier Transform Infrared Spectroscopy (FTIR) was employed for the study of the CNC – matix compatibility, while both Izod and tensile tests were performed for the evaluation of the mechanical reinforcement of CNC on LLDPE. X-Ray Diffractometry (XRD) measurements were performed for the determination of the structural properties of nanocomposites, while both Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were employed in order to study the effect of CNC on the LLDPE's thermal properties.

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Role of water molecules in the decomposition of HKUST-1

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Keywords: Metal organic frameworks, nitrogen adsorption, water vapour adsorption, methane adsorption, small angle X-ray scattering, small angle neutron scattering, effects of aging

The spectre of climate change concentrates minds wonderfully on alternative energy sources, and especially on their means of storage. The huge advantage of natural gas as a high energy/carbon ratio fuel is offset by the limited means available for its effective and safe storage. Adsorptive natural gas storage (ANG) could prove to be a solution to this problem, but a suitable adsorbent is lacking [1]. Metal organic frameworks (MOFs) of great gas adsorption capacity consist of transition metal ions or clusters bound together by organic ligands. They owe their excellent adsorption properties to their open framework with ordered pore structure and permanent porosity [2]. The fatal defect of many MOFs, however, is their poor long term stability in the presence of water vapour, due the weakness of the metal – ligand bonds [3].

Here we report a multi-technique investigation into the adsorption of water molecules in copper benzene-1,3,5-tricarboxylate (CuBTC MOF, Cu3(BTC)2 or HKUST-1). HKUST-1 is one of the most promising candidates to achieve the US DoE (Department of Energy) target (263 cm3 CH4/cm3 MOF at 35 bar) established for economical natural gas storage [4]. The present work investigates adsorption of water vapour by HKUST-1 using gas adsorption techniques (N2 and H2O uptakes are normalized with respect to water-free mass), thermogravimetry (TG), as well as small and wide angle X-ray scattering (SAXS and WAXS) and X-ray diffraction (XRD).

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STA/MS investigation of funcitonalized Graphene-based 2D materials

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Keywords: 2D materials, graphene, functionalization, thermogravimetric analysis, evolved gas analysis

2D materials and in particular graphene have become a prominent research topic in recent years. However, pristine graphene shows well known drawbacks, namely low reactivity, zero band-gap and limited dispersion in polar media, which restrict the span of applications and motivate research in its functionalization. These efforts resulted in a large variety of graphene derivatives with tunable features synthesized via covalent functionalization of graphene, starting mostly from fluorographene or graphene oxide.

Thermal analysis together with evolved gas analysis can provide important information about thermal stability of graphene derivatives as well as evaluation of the functionalization degree, at the same time helping to illustrate the different properties of the parent material and its derivatives. In our group several 2D materials were investigated in recent years using STA/MS analysis as a valuable tool. For example, in the case of controlled doping of graphene with nitrogen atoms, STA/EGA helped to identify the presence and chemical state of nitrogen adatoms/molecules [1]. Moreover, thermal analysis was used to study covalently functionalized MoS_2 with thiobarbituric acid (TBA), while providing information about TBA/Mo ratio, together with details about the thermal behaviour [2].

The present contribution is focused on STA/MS investigation of various graphene-based 2D materials carrying organic functionalities. For instance, the thermal analysis of heterobifunctionalized graphene containing FMP group helped to identify the presence of a covalent bond by increase in thermal stability after conjugation [3]. Alkynylated graphene, studied by STA/MS, shows mass losses attributed to phenylacetylene, 4-ethynyl aniline and 5-ethynyl pyrimidine functionalities respectively [4], thus highlighting the successful substitution. The combination of thermal analysis with other analytical techniques allows then to fully characterize the structure and properties of these advanced materials.

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The thermal conductivity of epoxy-boron nitride composites: effect of particle shape

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Keywords: epoxy, thiol, boron nitride, thermal conductivity, differential scanning calorimetry (DSC)

Boron nitride (BN) is widely used as a filler in epoxy resin systems in order to achieve high thermal conductivity while maintaining electrical insulation. The BN filler particles, as well as being of various sizes, may be in different forms, principally either as platelets or as agglomerates. Reports in the literature of the effect on the thermal conductivity of adding BN particles often do not make specific reference to the shape of the particles. In the present work we investigate this effect of BN particle shape on the thermal conductivity and cure kinetics of epoxy composites.

The epoxy system is based on a diglycidyl ether of bisphenol-A (DGEBA) epoxy crosslinked with a thiol, pentaerythritol tetrakis (3-mercaptopropionate), and a latent encapsulated imidazole (Technicure LC-80) is used as the initiator. The BN filler is in various forms: platelets with sizes of 2, 30 and 180 μm, and spherical agglomerates of size 120 μm. The epoxy and thiol are mixed in a stoichiometric ratio, the initiator is added in the proportion of 2 parts per hundred resin, and the BN filler is added in a proportion of 10, 30, 50, 60 and occasionally 70 weight% with respect to the weight of the epoxy and BN. The resulting composites contain volume percentages of BN of 3.7, 12.9, 25.7, 34.2 and 44.4%, the highest value being achieved only for the 30 and 180 μm platelets; for the other particles the mixture was an intractable paste with the 70% proportion of BN. Small samples were placed in aluminium crucibles for studying the cure kinetics by both non-isothermal differential scanning calorimetry (DSC), at rates of 2, 5 and 10 K/min, and isothermal DSC at cure temperatures of 60, 70 and 80 ºC. Larger amounts of these epoxy-thiol-BN mixtures were cast into silicone moulds and cured isothermally in an air-circulating oven to provide samples for the measurement of the thermal conductivity. The thermal conductivity was measured by the Transient Hot Bridge method.

The non-isothermal DSC results show that the cure of composites with 120 μm agglomerates, characterised by the peak exotherm temperature, is retarded by the addition of the BN particles, and increasingly so as the BN content increases. This behaviour lies intermediate between that for the 2 μm particles, for which the shift in the peak temperature is much greater, and that for the 30 and 180 μm platelets, which are very similar, and display a smaller shift. The isothermal DSC results show an initial decrease in the peak exotherm time as the BN content increases, followed by an increasingly rapid increase. Similar to non-isothermal cure, this is most dramatic for the 2 μm composites; for the 30 and 180 μm composites the shift is much smaller, while the composites with the 120 μm agglomerates closely follow the shifts of the larger platelets, but with a tendency to increase more dramatically at the higher BN contents.

The thermal conductivity of all the composites increases with BN content, but there is a significant effect of particle size, larger particles giving a higher thermal conductivity. For the platelets and 34.2 vol% of BN, for example, the values range from 1.28 to 3.02 W/mK for the 2 and 180 μm particles. This dependence mirrors the effect of the filler on the cure kinetics. The 120 μm agglomerates composites give a value of 3.42 W/mK for the same BN content, even higher than that for the larger 180 μm platelets. Comparison with earlier results for other BN particles [1] shows that composites with 120 μm agglomerates have a thermal conductivity which depends on BN content in a very similar way to that for 80 μm agglomerates, suggesting that agglomerates are more effective than platelets for increasing the thermal conductivity. The most noticeable effect, though, is for the smallest platelets, with a size of 2 μm, for which the cure kinetics is distinctly different from that for the other particle sizes, and for which the thermal conductivity is significantly lower.

Acknowledgments

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Thermal behaviour of inorganic nano filler in polymer nanocomposites

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Keywords: Thermal Analysis, Nanocomposites, SEM, XRD, TGA-DTA-DSC

Thermal analysis is one of the oldest technique for the analysis of materials for the test of materials to be genuine or fake, on the basis of simple heat test. Due to enormous advances in material sciences and day by day new materials are added up to the life of human being, so quality and perfection is highly in need with features such as low weight, high tensile strength, excellent physical and chemical properties, so thermal characterization along with other analytical techniques is an ideal tool for determining transition and materials properties.

In the present presentation, thermal studies based on my various research work performed on polymer nanocomposites of nanoparticles filler such as Calcium, barium, zinc, tin, silver will be highlighted taking matrix as polymer. Research work performed on polymer nanocomposites for material development using thermal analysis tool will also be discussed using the behaviors of Tg and Td with the increase in nanoparticles loadings in polymer matrix. Various analytical tool such as XRD, FTIR, SEM, EDS, and UV-Vis spectrum of Polymeric films of Nano composites will also be used for correlation and characterization of materials.

Cost-effective and green fabrication of 1D hollowed CNF spinel $NiCo_2O_4$ nanocomposite via dual nozzle electrospinning method

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Keywords: Carbon nanofiber, NiCo2O4, dual nozzle electrospinning, hydrothermal treatment

$NiCo_2O_4$ has been acknowledged as one of the most efficient and superior electrode materials towards energy storage applications due to its outstanding characteristics such as high theoretical capacity and richer redox reaction benefited from both Ni and Co cations. Unfortunately, up to date, single $NiCo_2O_4$ still suffers from poor rate capability and inferior cycling stability because of low electrical conductivity and small surface area. Thus, a well-organized architecture design of $NiCo_2O_4$ nanocomposite seems to be an effective solution. In this study, we fabricated 1D hollowed carbon nanofiber (CNF) fully decorated with spinel $NiCo_2O_4$ nanocomposite and used as an effective electrode towards supercapacitor application. 1D hollowed CNF was fabricated using dual concentric nozzle electrospinning method, comprising poly (vinyl pyrrolidone) (PVP) as soluble core and polyacrylonitrile (PAN) as shell. Electrospun PAN/PVP nanofiber mat was then soaked in the metal salts solution wherein PVP was leached out leaving a hollowed core, and then it was submitted into hydrothermal treatment. Lastly, prepared material was proceeded into two-steps calcination process under air and N_2 atmosphere, respectively. The hollowed structure of carbon nanofiber effectively boosted up the specific surface area of the nanocomposite, and the metal salts seeded around it promoted an overall 3D structure morphology which is beneficial to boost up the electrical conductivity and mechanical stability, leading to enhanced rate capability and superior cycling stability. Furthermore, electrospinning process in this study served as an effective method to fabricate uniform nanofibers, while eliminating the harsh conditions and high cost required in synthesizing commercialized carbon nanotubes.

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Thermal properties of nanohydrogel of poli(vinyl alcohol)/zirconium phosphate

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Keywords: hydrogel, PVAl, ZrP, intercalation, properties

Poly(vinyl alcohol) (PVAl) and nano lamellar zirconium phosphate (ZrP) were mixed in order to prepare a hydrogel for controlled drug release. ZrP was synthesized by hydrothermal method and then intercalated with oligoetheramine (OEA), at various ZrP:OEA ratios. The hydrogel was obtained by mixing aqueous solution of PVAl at 10% and disperions of pristine and modified ZrP in ethanol, at 60°C, under stirring. Following, the crosslinking was performed. Thermogravimetry (TGA), differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WADS) were used in order to evaluate hydrogel characteristics. PVA diffraction pattern changed due to the presence of ZrP. The ZrP *hkl* crystallographic plane disappeared indicating that intercalation of PVA inside the ZrP galleries occurred. Respect to the calorimetric properties, T_g and T_c showed slight changes and T_m remained constant. Crystallinity degree (X_c) changed for all hydrogels. ZrP increased the PVAl thermal stability.

Evaluation of thermal properties of mmcp composites with silver alloy matrix

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Keywords: silver matrix, MMCp composites, dilatometry, thermal analysis

A wide application of silver, silver alloys and composites with silver matrix in electronical and electrotechnical industry is mostly caused by good susceptance and thermal conductivity. These materials are mainly used as electric contacts, circuit-breakers and slide bearings. Contacts working conditions require meeting a number of requirements, amongst which the most crucial are: as high as possible thermal conductivity and susceptance, wear resistance during electric arc work, low susceptibility to tacking and chemical durability. Unreinforced silver alloys do not meet those expectations, hence the interest in composites with silver matrix is increasing. Reinforcing in shape of ceramic particles enhances resilience properties, improves adhesive and tribilogical wear resistance, it also minimizes formability, eliminates sparking. At the same time it worsens thermal conductivity and susceptance. Therefore, the type, size and volume fraction is selected so the decrease of susceptance and thermal properties of obtained composite (comparing with pure silver) was minimal with keeping advantageous performance.

In this paper, composites were examined, that were obtained with suspension method, which after casting were subjected to a plastic working in the process of extrusion. Materials reinforced with 10 % fraction of particles of reinforcing phase in the shape of glass carbon Gc, silicon carbide and aluminium oxide Al_2O_3 of 30 μm particle diameter were tested. It was stated that the presence of reinforcing phase of particles Al_2O_3, SiC and Gc influenced significantly on thermal conductivity. With addition of reinforcing particles, a decrease of thermal conductivity occurred in the composite of almost 250 % comparing to that of pure silver. Operating temperature of electric contacts made from composites of alloy matrix is about 450 °C. Thermal analysis confirmed that up to this temperature, no significant changes occurred that could influence on contact work. Dilatometric studies helped to determine an influence of particle type of reinforcing phase on thermal expansion of composites in temperature ranges of work of those materials. Based on obtained results, the evaluation of influence of reinforcing phase type on selected thermal properties of composites with silver matrix was performed.

Acknowledgments

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Thermal transformations during fabrication by reactive sintering of Aluminum-based hybrid composites

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Keywords: Al-based composites, reactive sintering, thermite reaction, DSC

An innovative fabrication method based on powder metallurgy techniques was developed for aluminium-based composites. A fraction of 20 % vol. of alumina (Al_2O_3), particle size <0.3 µm, was used as embedded reinforcement. An additional fraction of *in-situ* nano-sized reinforcement was produced by mean of the thermite reaction between aluminium matrix and 7.5% vol. ferrous oxide (Fe_2O_3) powder, particles size <40 nm. The blend of powders was mixed under argon protection and hot-pressed into 10x5mm compacts for 5 minutes at 350°C. Similar compacts with only 20 % vol. of ex-situ alumina and no ferrous oxide were used for reference. An extensive investigation program of DSC analysis was performed as isochronal heating with rates between 5 and 30°C min^{-1} to determine the optimum parameters of the subsequent sintering treatment. The very complex appearance of DSC curves for hybrid composites evidenced a variety of superposing reactions, which could be attributed to phase formations or decompositions, oxidations phenomena, and melting. Experimental DSC curves were mathematical analysed to separate the different thermal reactions that occurred, using the first derivative method, and resulting peaks were fitted using the general Gaussian model. The resulting exothermic reactions that resulted below 650°C and were not evidenced on reference Al-Al_2O_3 composites, were put in connection to the thermite reaction of ferrous oxide with aluminum and formation of secondary alumina, as well as some other Al-Fe phases. Based on these results, the optimal sintering temperature was set at 650°C. Investigations of X-rays diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) were performed to evidenced complete decomposition of Fe_2O_3 particles during the sintering treatment and formation some new phases. The Kissinger method was also used to determine de activation energies, which were compared with some previous results on similar hybrid composites fabricated using micron-sized Fe_2O_3 particles [1].

Illustrations

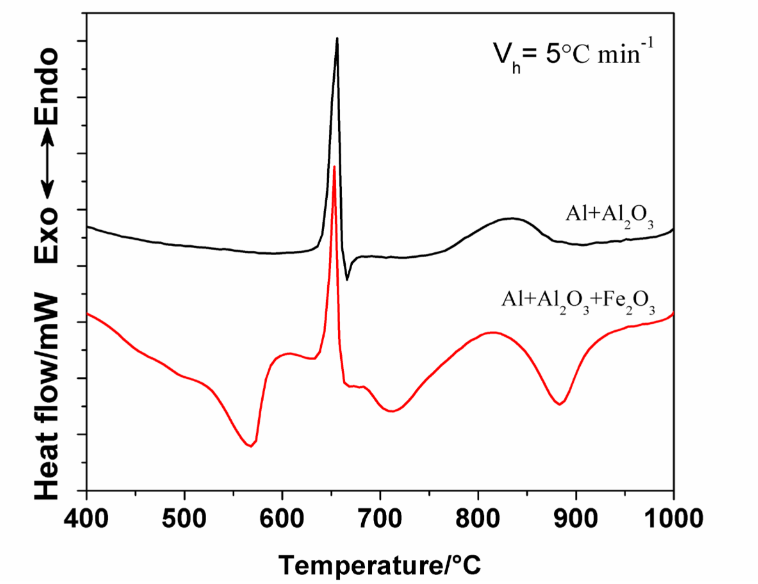

Fig. 1 DSC curves of hybrid composite Al+Al_2O_3+Fe_2O_3 and reference Al+Al_2O_3 at 5° min^{-1} heating rate.

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Thermal properties and degradation kinetics of polyoxymethylene/functionalized hydroxyapatite composites

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Keywords: Nanocomposites, Polyoxymethylene, Hydroxyapatite, PCL, Grafting,

Polyoxymethylene (POM) belongs to the biocompatible and biostable polymers with high strength and stiffness, biological inertness, resiliency, toughness and low friction coefficient [1]. Hydroxyapatite (HAp), seems to be an ideal material to develop bone tissue engineering scaffold due to its osteoconductive and osteoinductive properties as well as the close structural composition to natural bone [2]. However, the biggest disadvantage of POM is its poor thermal stability. At elevated temperatures it readily undergoes thermal decomposition. Furthermore, POM tends to follow an “unzipping” process with emission of formaldehyde molecules [3]. Our previous studies show that addition of functionalized hydroxyapatite leads to increase POM thermal stability [4].

In the presented study hydroxyapatite was chemically modified by poly(ε-caprolactone) (PCL) using diisocyanate as a coupling agent in a grafting reaction and then incorporated into POM matrix using melt processing methods. The obtained POM/HAp-g-PCL composites were investigated using DSC, TOPEM DSC and TG. The highest degree of crystallinity were found for POM/1% HAp-g-PCL system which suggests that HAp-g-PCL can act as a nucleating agent in the POM crystallization process. Importantly, in the contrast to unmodified HAp, HAp-g-PCL significantly increases the POM thermal stability. Kinetics of POM thermal degradation have been calculated using Friedman method and the best mathematical model of kinetic function has been found using non-linear regression method.

Acknowledgments

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The effect of phase change materials on thermal properties of polyurethanesaccharides modified with magnetite

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Keywords: polyurethane, magnetite, phase-change material, poly(ethylene glycol), hydroxyapatite

Polyurethanesaccharides-based (PUS) composites have a great potential in biomedical applications including bone cements and hard tissue replacements [1]. Hydroxyapatite (HAp) is the most frequently used additive to bone implants and cements due to its chemical similarity to inorganic part of human bones; additionally HAp is increasing their bioactivity [2]. On the other hand, the introduction of magnetic nanoparticles (MNPs) into polymer matrix can enhance mechanical, thermal and magnetic properties of polyurethane nanocomposites [3]. The main problem with polymeric bone cements is the high temperature reached during the curing process. One of the methods to reduce the polymerization temperature of acrylic bone cements is addition of phase-change materials (PCM) that can accumulate heat released during curing of bone cements [4].

In the presented study PUS, modified with hydroxyapatite, magnetite and poly(ethylene glycol) (PEG) with average molar mass 8000 as phase-change material (PCM), have been proposed as a potential new polymeric bone cements. The polyurethanesaccharide/magnetite/hydroxyapatite nanocomposites have been prepared in a two-step bulk polymerization process. PUS were obtained using 1,6-hexamethylene diisocyanate (HDI), poly(ethylene glycol) (PEG) with average molar mass 2000, 1,4-butanediol (BDO) as a chain extender, sodium alginate as cross-linker and a chain extender in stoichiometric amounts. Poly(ethylene glycol) (PEG) with molar mas 8000 was applied as PCM to decrease the temperature of polymerization.

From TG and DSC data it can be found that both magnetite and HAp changes the thermal stability and thermal properties of PUS nanocomposites. Additionally, thermogravimetric analysis show that the presence of magnetite increases thermal stability of PUS matrix. The influence of additives on the glass transition region of PUS matrix has been investigated by DMA method and it was found that glass transition temperature was slightly decreased by magnetite presence. It was confirmed that incorporation of PCM effectively decrease maximum curing temperature of PUS-based systems.

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The authors are grateful to the Polish National Science Centre for financial support under the Contract No. UMO-2016/22/E/ST8/00048.

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Thermal analysis evaluation of pmma doped with [Eu(tta)$_3$(H$_2$O)$_2$] and [EU(tta)$_3$(TPPO)$_2$] complexes and nanosilver

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Keywords: separate europium, luminescence, nanosilver, PMMA

In this work is reported in this work the preparation, characterization and photoluminescence study of poly(methylmethacrylate) (PMMA) thin films co-doped with [Eu(tta)$_3$(H$_2$O)$_2$] and [Eu(tta)$_3$(TPPO)$_2$] complexes. Both the composition and excitation wavelength may be tailored to fine-tune the emission properties of these Ln3+–b-diketonate doped polymer films, exhibiting red primary colours. The introduction of metallic nanosilver (Ag°) in the luminescent system of PMMA- Eu complex showed an unprecedented intermolecular energy transfer process, in which transfer improved luminescence effect regarding Eu^{3+} ion. The PMMA polymer matrix acts as a co-sensitizer and enhances the overall luminescence intensity of the polymer films. Furthermore, it provides considerable UV protection for the luminescent species and improves the photostability of the doped system according to thermal analysis evaluation. Thermogravimetry analysis (TGA) showed no weight loss in the range of 323–473 K for the polymeric systems, suggesting that the interaction between the polymer matrix and the Eu^{3+}-complex occurs when the carbonyl groups along the polymer backbone substitute the water molecules in the complex precursor.

Acknowledgments

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Thermal behaviour of organically modified vermiculites

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Keywords: vermiculites, thermal analysis, FT-IR spectroscopy, X-ray diffraction

The organically modified clays have achieved a broad range of application in many areas: environment protection (immobilization of contaminants), pharmacy, electrochemistry, packaging storage, ceramics etc. Interactions between organic compound and clay mineral leads to a formation of the dispersed organic and inorganic component in nanometer dimensions, which causes properties different from those of the original components (e.g. better mechanical properties, higher thermal stability, lower flammability, easier biodegradability of polymers etc.) [1-4]. The vermiculite samples were modified by different types of alkylammonium cations by sorption procedure. Thermal behaviour of the organically modified vermiculite was investigated by simultaneous thermogravimetry and differential thermal analysis. The modification of vermiculite caused changes of the temperatures of dehydratation and dehydroxilation processes as well as total melting process in the temperature interval from 25 to 1000 °C. X-ray powder diffraction was used to calculate the values of basal space of the modified vermiculite to confirm the intercalation of alkylammonium cations into the vermiculite structure. The nature and modified vermiculite were also characterized by means of FT-IR spectroscopy which proved sorption or intercalation of the alkylammonium cations too.

Acknowledgments

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Influence of stoichiometry and graphene addition in a dynamic epoxy network

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Keywords: epoxy, dynamic network, stoichiometry, graphene

In this work we analyse the influence of stoichiometry and graphene addition in the curing and properties of an epoxy network containing phenyl disulphide moieties. Recently a new epoxy vitrimer [1] has been used as matrix in fibre composites. This epoxy vitrimer is obtained through the reaction of diglycidyl ether of bisphenol A (DGEBA) with 4-aminophenyl disulphide (AFD), giving rise to a "dynamic" epoxy network, which has reversible crosslinks based on aromatic disulphide bonds. These characteristics offer the possibility of reprocess, repair and recycling.

The epoxy matrices of diglycidyl ether of bisphenol A (DGEBA) and 4-aminophenyl disulphide (AFD) as crosslinking agent were prepared with different amine/epoxy ratios. Epoxy-graphene nanocomposites were prepared using three types of graphene with similar nanoplatelet dimensions: unfunctionalized graphene (GNP) and functionalized with amine groups (GNP-NH_2) and with carboxylic groups (GNP-COOH).

The curing of DGEBA-AFD and graphene/DGEBA-AFD dispersions was studied by Differential Scanning Calorimetry (DSC). Thermal and dynamic-mechanical properties of epoxt thermoset and graphene nanocomposites were studied by and Dynamic Mechanical Thermal Analysis (DMTA).

The DGEBA-AFD reaction becomes faster in excess of amine groups, as expected the reaction enthalpy reached maximum values near the stoichiometric ratio, and the formed thermoset present the highest T_g for the stoichiometric ratio. This behaviour is similar to the one found for DGEBA crosslinked with diamine diphenyl methane [2]. Therefore the presence of disulphide bonds does not modify the epoxy curing behaviour. Moreover DMTA experiments evidenced that T_g and rubbery modulus ($T>T_g$) reached maximum values at the stoichiometric DGEBA-AFD ratio, showing a lower degree of croslinking in non stoichiometric neworks.

The curing of graphene/epoxy dispersions proceds faster than neat epoxy indicating that graphenes slightly acelerate the curing reaction, while no changes in the heat of reaction were observed.

The presence of graphene lowers the T_g of the epoxy matrix which indicates the formation of non-perfect epoxy networks. Graphene/epoxy nanocomposites show increases in the storage modulus E' in both the glassy region ($T<T_g$)) and in the rubbery region ($T>T_g$). A peculiar behaviour was found in tanδ-temperature curves wich show shoulders at temperatures lower $\tan\delta_{max}$ which may reflects microdomains present on the epoxy matrix.

Finally, the contact angles (advance and retreat) of water were measured on epoxy samples loaded with graphene nanoparticles to study the hydrophobicity of the materials, which was similar in all of them being slightly higher in GNP-NH_2/epoxy nanocomposites.

Acknowledgments

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Boron Nitride/epoxy resin Nanocomposites: Development, Characterization and Functionality

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Keywords: thermo-mechanical response, dielectric relaxation, energy storage, multifunctionality

Polymer matrix composites with embedded ceramic nanoparticles receive enhanced scientific and technological interest, because of their improved thermo-mechanical, electrical, magnetic and other properties [1-3]. This type of materials, is a promising new class of engineering materials for applications such as stationary power systems, cellular phones, wireless personal digital assistants and hybrid electric vehicles. Ceramic/polymer nanocomposites exhibit multifunctional performance since they are able to combine structural integrity and appropriate thermal response with tunable dielectric behaviour [4-6].

Materials' multifunctionality refers to the combination of various desirable properties in a system, aiming to develop a single material/system which will be able to exhibit all necessary responses under various loading conditions at service. Mechanical sustainability, suitable thermal response, tunable electric conductivity, variable electric polarization and dielectric permittivity, magnetic properties, thermally induced phase changes could be parts of the overall multifunctional behaviour.

Epoxy resins (ER) are suitable matrices for the development of high tech nanocomposites because of their thermo-mechanical stability, low shrinkage, resistance to corrosion, strong adhesion with nanoparticles and low cost. Boron nitride (BN) is a two-dimensional material with high chemical and heat resistance. In this study BN/ER nanocomposites have been prepared and studied varying filler loading. Morphology of the prepared samples has been examined by means of scanning electron microscopy (SEM), followed by thermal characterization via differential scanning calorimetry (DSC). Structural integrity of the nanocomposites was investigated by means of dynamic thermal mechanical analysis (DMTA) from ambient to 160°C. Broadband dielectric spectroscopy (BDS) was employed in order to study the electrical properties of the manufactured nanosystems, with parameters the filler content, the frequency of the applied field and the temperature.

Results indicate fine dispersions of nanoparticles within the polymer matrix and enhancement of mechanical response with filler content. Moreover, relaxation phenomena were detected with DMA and BDS measurements. Thermosetting matrix undergoes glass to rubber transition upon heating, while a secondary process recorded via BDS concerns the re-arrangement of polar side groups of the main polymer chain. Nanoinclusions contribute to the dielectric response of the systems with interfacial polarization which occurs via the charge built up at the interface of the constituents. Finally, they ability to store energy and the effect of BN content upon the thermo-mechanical and dielectric behaviour of the nanocomposites is examined and discussed.

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Preparation and thermal performance of PEG/GO composite phase change materials by electrospinning

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Keywords: phase change materials, electrospinning, preparation, thermal performance

To solve the poor thermal conductivity of organic phase change materials (PCMs), graphene oxide (GO) with outstanding thermal conductivity and excellent mechanical properties, was used as a thermal conductive reinforcement component to prepare a novel composite solid-solid PCMs. The novel composite solid-solid PCMs were prepared using PEG as PCMs, PVP as matrix spinning solution and GO as the thermal conductive reinforcement component through electrospinning. Scanning electron microscopy shows that the composite PCMs were nano-fibers with smooth surface. Differential scanning calorimetry confirms that all the composite PCMs with different content of GO possess good phase change behavior and their latent heat of melting can achieve 90.6 J/g as the content of GO is 0.5 wt%. The X-ray diffraction patterns indicate that the PEG chains in the composite PCMs maintain their crystalline behavior and show two strong characteristic peaks at 19^{o} and 23^{o}, which ensure the good phase change behavior for the composite PCMs. Therefore, this research provides a new method to prepare composite PCMs and the novel composite PCMs possess potential applications in thermal energy storage systems.

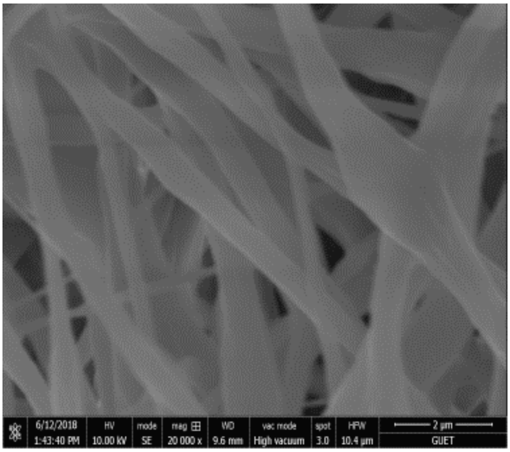

Fig.1 SEM images of the composite PCMs

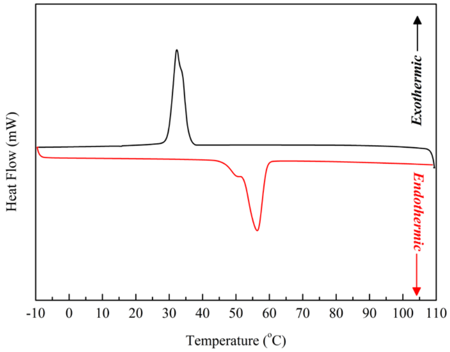

Fig.2 DSC curves of the composite PCMs with 0.5 wt% GO

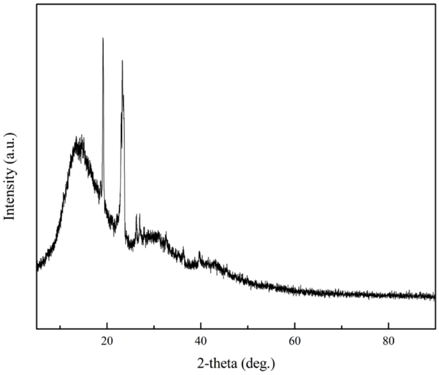

Fig.2 XRD pattern of the composite PCMs with 0.5 wt% GO

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Effect of graphene nanoplatelets loading on the thermal properties of crosslinked polyethylene/graphene nanocomposites

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Keywords: crosslinked polyethylene, graphene nanoplatelets, nanocomposites, thermal properties

Crosslinked polyethylene (PEX) materials have been successfully used in domestic hot and cold water piping due to their good properties such as high temperature strength, good elastic modulus and high impact resistance [1]. Different types of graphene such as graphene oxide, graphene nanoplatelets (GNPs), are often used as a multifunctional reinforcement filler material to improve the electrical, mechanical, gas barrier and thermal properties of a polymeric matrix [2]. The aim of this work is to produce reinforced PEX/GNPs composites with increased thermal conductivity suitable for geothermal piping system. For this reason, PEX/GNPs nanocomposites were prepared by the melt mixing method using GNPs with 5μm in diameter and 6nm in thickness at various filler's concentration (0.5, 1, 2.5, 5% wt.). The structural characterization of neat PEX and the corresponding nanocomposites was studied by using X-Ray Diffraction (XRD). The crystallinity of PEX/GNPs nanocomposites was calculated by Differential Scanning Calorimetry (DSC) while the thermal stability of the samples was examined by Thermogravimetric Analysis (TGA). The thermal conductivity of the PEX and its nanocomposites was measured by a device which is based on the hot/cold tank principle [3]. Finally, mechanical properties testing was performed in order to determine the influence of the filler's content on Young's modulus, tensile strength and elongation at break of PEX matrix. TGA results and tensile testing showed that the nanocomposites exhibited better thermal stability and increased Young's modulus than neat PEX.

Acknowledgments

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Organic materials

Structural similarity and similarity in thermal properties of the polymorphs of tolbutamide and chlorpropamide

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Keywords: polymorphism, active pharmaceutical ingredients, phase transition

The polymorphism of molecular crystals remains a hot topic for several decades, and the polymorphism of active pharmaceutical ingredients (API) is of utmost importance. Tolbutamide (TB) and chlorpropamide (CPA) are two API (both curing type 2 diabetes), with alike molecules. For today, sixteen polymorphs of these substances were solved, seven for tolbutamide and nine for chlorpropamide. All crystal structures of TB and CPA that were solved for today possess a single structural motif – infinite hydrogen-bonded ribbons. The infinite hydrogen-bonded ribbons can be arranged in two types, thus increasing the variety of the polymorphs. For CPA, these two types look like z- and π-shaped configurations. Two similar types of the ribbons can be identified in TB. Similarity in the structure is accompanied with the similarity in thermal properties. One can summarize two pairs of polymorphs behaving in the same way in both substances. The first pair is the polymorphs most stable near the melting point, ε-CPA and I^H TB. The second pair is the polymorphs crystallizing most readily from their melt, β-CPA and V TB. Surprisingly, the polymorphs in the pairs also turned out to be very similar in their crystal structures. Under heating, all tolbutamide/chlorpropamide polymorphs transform into high-temperature I^H/ε polymorph, which melts at 128 °C [1-3]. The crystal structures of the high-temperature polymorphs are very similar to each other in the unit cell parameters and in the arrangement of z-shaped infinite hydrogen-bonded ribbons. The similarity between the structures and thermal properties of these pair polymorphs is spread onto another their common point, reversible conformational transformations into low-temperature polymorphs ($I^H \leftrightarrow I^L$, $\varepsilon \leftrightarrow \varepsilon'$) [3]. Both transformations are single-crystal to single-crystal. Under cooling, other polymorph crystallizes from the melt, V for tolbutamide and β for chlorpropamide. Both crystallized polymorphs are metastable, and then transform into other more stable polymorphs. Solid-solid transformation V → II in tolbutamide was detected. The polymorphs of tolbutamide and chlorpropamide crystallized from their melts turned out to be also very similar to each other in their structures (space group, unit cell parameters, arrangement of π-shaped infinite hydrogen-bonded ribbons). It seems reasonable that the case of tolbutamide-chlorpropamide pair is not unique, and other pairs or even more numerous groups can be found among molecular crystals (API). If so, such a "group approach" to the investigations of molecule crystals can make the screening of polymorphs more effective and less labor. At least, if evident similarity is found among the polymorphs of similar molecules in their crystal structure, one can expect and check the similarity in their thermal properties.

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Thermal elimination study on pore-templating surfactants

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Keywords: cetyl trimethyl ammonium bromide, Pluronics 10300, evolved gas analysis, TG-MS, TG-FTIR

Application of ionic and non-ionic surfactants as pore templating agents is usual in preparation of mesoporous silica coatings [1-3]. The most frequently applied template is cetyl trimethyl ammonium bromide, CTAB, beyond various nonionic triblock copolymers [4-6]. We were going to utilize them in preparation of nanostructured antireflective bilayers [7].

Thermal behaviour and thermal elimination processes of the cationic tenside, CTAB and one of the triblock copolymers, Pluronics® PE10300 has been reviewed and studied in details by both TG/DTA-MS and TG-FTIR-gascell measurements at constant heating rate of 10°C/min. Their thermal degradation and decomposition have been followed by the two evolved gas analytical methods in comparison. The complexity of thermal processes has been also compared to those of occurred in the combination with silica sols during their joint calcinations.

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Thermal properties of residue composites from coffee capsules with sugarcane bagasse fibers

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Keywords: coffee capsule, sugarcane bagasse, thermal analysis

In recent years, several kinds of coffee capsules have been introduced the market over, all of them falling into two main capsules' categories: aluminum and plastic. Around 10,000 tons of coffee's capsules were consumed in 2017 in Brazil, and it is expected to catch up 14,000 tons in 2021. However, one of the threats associated with the increasing usage of capsules is the environmental impact that it can be caused by the packaging materials. Vegetal fibers have been highlighted as reinforcement in polymeric matrix composites, in view of their natural abundance. Thus, the aim of this study was to investigate the thermal properties of composites obtained from coffee capsules residues with addition sugarcane bagasse fibers, developed as a sustainable solution for these waste management. The sugarcane bagasse was dried in oven at 60 °C for about 24 h and then it was milled in a knife mill coupled with 2 mm sieve. Furthermore, the fiber was treated with a 4 % (m/v) NaOH solution by stirring at room temperature for 1 h. The disposed capsules were cleaned to remove the coffee grounds. The composites were obtained by using a mini-extruder (HAAKE Mini Lab II, Thermo Scientific) at 190 °C for 8 min and screw speed of 60 rpm. The samples were prepared containing 5% and 10% (w/w) of sugarcane bagasse (untreated and treated with 4% NaOH solution), with or without addition of 2 % (w/w) compatibilizer. Thermal characterization by TG/DTG and DTA analysis was performed on TA Instruments equipament, SDT Q600 model, with heating rate of 10 ˚C min^{-1}, temperature range from 25 to 600 °C under nitrogen atmosphere (flow rate of 120 mL min–1). The TG analysis showed all these composites to present a relatively good thermal stability. The composites prepared with 5% (w/w) of sugarcane bagasse, untreated, had very like behavior the neat polymer between 250 and 450 °C. The DTG curves showed that the maximum mass loss occurred at 465 °C, for neat polymer and its composites. DTA curves for all composites and neat polymer showed the presence of two endothermic events at both around 160 and 430 °C, referring to polypropylene melting temperature (T_m) and its decomposition. DTA curves also showed a slight difference in profiles between 180 and 400 °C. All the composites showed glass transition temperatures different (T_g). The composite with 10% (w/w) of treated fiber with addition of compatibilizer showed the lower T_g (4.2 °C). The other samples showed temperature higher than de neat polymer reaching to 8.4 °C.

Pharmaceuticals

Doxorubicin-loaded nanostructured lipid carriers functionalized with folic acid for the treatment of breast cancer

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Keywords: Breast cancer, doxorubicin, nanostructured lipidic carrier

Breast cancer is a serious public health problem that causes thousands of deaths annually. Doxorubicin (DOX) represents one of the most active and effective compounds used in clinical practice. Commercial formulations using nanostructured systems based in liposomes exhibit physico-chemical instability and low specificity. Thus, DOX loaded in a nanostructured lipid carrier (NLC) is a promising alternative. These systems present better stability than liposomes and the selectivity can be improved by the functionalization of the NLC with a targeting moiety. Thus, in this work, a DOX-loaded NLC formulation was proposed. Folic acid (FA) was chosen to functionalize the NLC, in order to allow the selective delivery of the drug in tumor tissues that overexpress folate receptors. The first step of this work consisted in the chemical attachment of FA to the poloxamer 407in the development of NLC. Infrared spectrometry, nuclear magnetic resonance spectroscopy and differential scanning calorimetry techniques indicated that the carboxyl groups of the FA and polymer reacted resulting in a new ester bond. Subsequently, it was possible to develop DOX-loaded NLC-FA with average size smaller than 170 nm and stable for more than 90 days, as demonstrated by dynamic light scattering and scanning electron microscope technique. *In vitro* release experiments revealed that the release of DOX-NLC cationic particles and DOX-NLC particles were similar, reaching 100% released after 12h. Finally, cytotoxicity was investigated in a MCF-7 cell line and the results demonstrated that DOX free and DOX-loaded in NLC-AF (46 micromolar concentration) reduced viability by 54 and 90% respectively demonstrating that the DOX-loaded NLC-AF is more effective than DOX free. *In vivo* studies will be conducted in the future to investigate tumor targeting of the particles and confirm the potential of this new nanotech strategy.

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Thermal behavior of anti-inflammatory drug naproxen

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Keywords: Naproxen, Thermal decomposition, Evolved gases analysis.

Naproxen (NAP) ((+)-(*S*)-2-(6-methoxynaphthalen-2-yl) propionic acid) is non-steroidal anti-inflammatory (AINES) drug, that presents anti-inflammatory, anti-thermic and analgesic action related to the inhibition of cyclooxygenase enzymes COX1 and COX2. These enzymes catalyze the production of prostaglandines, which are lipids physiologically active that induce the inflammation process.[1] The combination of thermal analysis with complementary spectroscopic techniques permits detailed investigation on thermal behavior of several materials including drugs. Such studies involves thermal decomposition, thermal stability, reactions in solid state, purity of drugs, physical transformations, polymorphic transitions, melting point, crystallization, evolution of gases, among others changes.[2-5] Some previous reports about thermal analysis of naproxen can be found, however, none of them proposed a thermal decomposition mechanism to this drug.[6-11] Therefore, in this report thermal analysis techniques, TG/DTG/DTA, DSC and TG-FTIR, were used to detailed investigation of thermal properties of NAP to propose a mechanism of its thermal behavior. The results obtained by TG/DTG in N_2 presented a single mass loss step, assigned to the decomposition of the drug between 153.5 and 305.2 °C, without residue at the end of the run. In DTA curve, it was observed a sharp endothermic peak related to melting of NAP, at 156.6 °C. Others endothermic and exothermic peaks were also observed, associated to the decomposition process. DSC curves of NAP were recorded in the heat-cool-heat mode. In the first heating a sharp endothermic melting peak was observed at 156.7 °C. In the cooling cycle it was observed one exothermic peak at 99.0 °C representing the recrystallization of the drug. During the second heating an endothermic peak at 154.8 °C suggests the reversibility of this process. Therefore, it was calculate the first heat $\Delta_{fus}H = 31.57\ \mathrm{kJ\ mol^{-1}}$ / $\Delta_{fus}S = 73.44\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and second heat $\Delta_{fus}H = 29.49\ \mathrm{kJ\ mol^{-1}}$ / $\Delta_{fus}S = 68.92\ \mathrm{J\ K^{-1}\ mol^{-1}}$, revealing less crystallinity in the second melting. The gases evolved during heating of naproxen were characterized by TG-FTIR. Thus, high intensities were observed at 65 min, which correspond to 673.2 °C. The interpretation of the spectra was realized using NIST Database and EPA Vapor Phase databases for comparison.[12-13] . Bands related to 2-methoxynaphthalene and propionic acid were clearly observed in the gas phase demonstrating that naproxen decomposes via releasing of these substances. Therefore, the interpretation of data allowed to suggest a proposed mechanism of thermal decomposition.

Acknowledgments

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Thermal decomposition mechanism of doxycycline

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Keywords: Tetracycline, Doxycycline, Evolved gas analysis

Tetracyclines (TCs) are a group of bacteriostatic antibiotics widely used in the treatment of bacterial infections in both human and veterinary medicines, due to its action against Gram-positive and Gram-negative bacteria[1]. The biological action is due to the binding of the pharmaceutical to the bacterial ribosome. In addition these antibiotics present low toxicity, low cost, and can be orally administered [1]. Between 1950 and 1970, various antibiotics of tetracycline family were developed and became the most used pharmaceuticals in EUA to combat infectious diseases and they are long lasting in environment [2].

Thermal analysis permits the evaluation of several aspects of the pharmaceutical compounds, including thermal stability, polymorphism, drug-excipient interaction studies, melting, crystallization and many others, including the characterization of thermal degradation products that may guide an eventual disposal. [3]

This work aims to investigate the thermal behavior of doxycycline monohydrated, including gases evolved during its heating by TG-FTIR, proposing a tentative mechanism of its thermal decomposition in order to map the drug behavior since sub-ambient temperatures up to its degradation.

The evolved gas analysis was carried out using a SDT-Q600 modulus (TA Instruments), coupled with a Nicolet iS10 FTIR Spectrometer. The transfer line consists of a stainless steel tube 120 cm in length and 2 mm in inner diameter, heated at a constant temperature of 230 °C. FTIR measurements were carried out with a DTGS detector in a gas cell, heated at a constant temperature of 250 °C. The interferometer and the gas cell compartments were purged with nitrogen, also used as purging gas flowing at 50 mL min^{-1}, heating rate of 10 °C min^{-1} and sample mass of *c.a.* 16 mg.

TG curve, in nitrogen, presented three steps of mass loss. The first one from room temperature to 147 °C, followed by a second mass loss between 157 a 382 °C and finally the sample pyrolyses from 382 until the end of the run, with mass losses of 4.5, 33.6 and 22.4%, respectively, leading to a final residue of 40%. DTA curve presented two endothermic peaks at 132 °C related to dehydration and at 174 °C referent to doxycycline melting [4]. An exothermic peak was observed at 209 °C due to the sample decomposition.

DSC curve of the drug revealed two endothermic peaks at 151.1 and 174.6°C, related with dehydration and melting ($\Delta_{fus}H = 37.0$ J g^{-1}) respectively.

Evolved gas analysis indicated the maximum evolution of volatiles at 205, 315, 435, 475 and 535 °C. FTIR spectra collected at these times were compared to database spectra [5] and revealed the release of isocyanic acid, dimethylamine, water, carbon dioxide, ammonia, methane and carbon monoxide. According to previous work, part of carbon dioxide and ammonia are products of decomposition of isocyanic acid. [6]

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Lorazepam-nicotinamide co-crystals formation via mechanical grinding

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Keywords: co-crystal, mechanical grinding, lorazepam, nicotinamide

Physicochemical properties of active pharmaceutical ingredients (APIs) are key factors in drug development. Poor solubility in water, slow dissolution rate or low stability of APIs could limit their performance in medicine. Therefore searching for ways of APIs physicochemical properties modifications is a challenging and interesting issue for a broad spectrum of pharmaceutical technologists. One of the promising ways could be co-crystal formation [1]. Co-crystals are described as single, neutral, crystal phase composed of two ingredients (mostly API with neutral component) connected via non-covalent bond. Co-crystals could be formed mainly using two routes, i.e., solid-state and solvent-assisted methods. Solid-state methods base on grinding substances in mortar or mechanical grinders. The grinding could be carried out without solvent (net-grinding method) or with addition a few drops of organic solvent (liquid-assisted grinding method). Slurry conversion, solvent evaporation, anti-solvent addition are examples of solvent-assisted methods. Mechanism of co-crystal formation is not fully understand [2]. Molecular diffusion, intermediate amorphous state or eutectic mixture formation are considered as mechanisms of co-crystallization via co-grinding. Also impact of small amounts of solvents addition in liquid-assisted methods is still debated. Spectroscopic (FTIR and Raman) and thermal (DSC) approaches were used to investigate formation mechanism and to in-line monitoring of co-crystallization process [2–4].

In the study lorazepam was chosen as a model API. Lorazepam is potent benzodiazepine drug used in status epilepticus, for pre-anesthetic medication or chemotherapy-induced nausea. Poor water solubility and extensive metabolism in liver to pharmacologically inactive glucuronides are crucial problems associated with lorazepam administration [5]. Therefore screening of possibility of co-crystal formation with lorazepam were studied. The preliminary researches suggest possibility of co-crystallization of lorazepam with nicotinamide.

The purpose of the study was to investigate the mechanism of co-crystal formation between lorazepam and nicotinamide via grinding route (neat and liquid assisted). The properties of potential co-crystals obtained by mechanical grinding were compared with those prepared by slow solvent evaporation method. For this reason, lorazepam-nicotinamide physical mixtures were ground in mechanical grinder using agate balls without or with small amount of methanol. In settled time interval (1 min, 5 min, 10 min, 20 min, 30 min, 45 min, 60 min) the grinding was stopped and obtained product was allowed to evaporate at ambient condition for 24 h. Solvent evaporated samples were prepared by dissolving both ingredients (lorazepam and nicotinamide) in methanol, heated if necessary, then obtained product was allowed to evaporate at ambient condition. These two groups of potential co-crystals were analyzed using thermal method (DSC) and spectroscopic methods (FTIR and Raman). The findings of the study revealed the possible mechanism of co-crystallization occurred between lorazepam and nicotinamide.

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Thermal study of lorazepam-nicotinamide co-crystals

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Keywords: co-crystal, lorazepam, nicotinamide, DSC

Introduction into the pharmaceutical market the efficient, safe and comfortable for patients drug dosage forms requires a complete recognition of physicochemical properties of active pharmaceutical ingredients (APIs). The investigation program comprises, for instance, characterization of the phase transitions of API, its water solubility and degradation under heat, moisture or light. The most important problem in the pharmaceutical technology is that over 60% of APIs is very slightly soluble or practically insoluble in water. Thus, optimization of undesired physicochemical properties of APIs is one of the main challenges in drugs development process since poor water solubility and slow dissolution rate influences the API bioavailability. This emphasises the importance of seeking new ways of modifying the water solubility of active substances. Among these ways co-crystallization gain growing interest.

Co-crystal formation could improve the physicochemical properties of benzodiazepines without changing their chemical entities. It is possible due to co-crystallization of benzodiazepines with neutral compound (so-called “coformer”), both are hold together in the same crystal lattice via the noncovalent bond, in most cases hydrogen bond [1,2]. Thermal methods are one of the most important techniques in screening and confirmation of co-crystal formation. The study of drug substance binary mixtures with co-former using DSC allows the prediction co-crystal formation [3]. Moreover, thermal stress could induce co-crystallization process [4]. Therefore, the main scope of the study was the thermal investigation of lorazepam-nicotinamide co-crystals. Lorazepam is the benzodiazepine derivative drug substance with anxiolytic and sedative properties used to treat status epileptics, insomnia, anxiety disorder. It is a poorly water soluble drug substance that belongs to class II according to BCS classification system [5].

In the first stage of the study lorazepam physical mixtures with nicotinamide were prepared at the molar ratio 1:1 using automatic agitator. DSC technique with different heating rates, i.e., 2°C/min, 5°C/min and 10°C/min. were used to investigate these mixtures. In the next stage of the study, the binary mixtures were examined under heating-cooling program to investigate possibility of inducing co-crystal formation by thermal stress. Binary mixtures were heated to settled temperature (about 150°C), cooled and then again heated (heating rate 2°C/min, 5°C/min and 10°C/min). Then binary mixtures of lorazepam with nicotinamide at different molar ratios were prepared to study phase diagram of lorazepam-nicotinamide system. The study allowed to deep insight in formation of co-crystal between lorazepam and nicotinamide depending on heating rate. Construction of phase diagram allows to distinct co-crystals from eutectic mixture.

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Effect of plasticizer type/quantity on the thermal behavior of acetic acid and citric Acid-based chitosan films

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Keywords: Chitosan, Mucoadhesive films, Citric acid (CA), Plasticizer.

Chitosan is a cationic polymer having advantages such as mucoadhesivity, high biocompatibility, biodegradability and ease of chemical modification. It is a weak polymer base, soluble in aqueous acidic media to produce a highly viscous solution suitable for making films [1]. Mucoadhesive drug delivery involves different sites covered by mucosa, such as gastrointestinal, oral cavity, nasal, ocular, vaginal and rectal drug delivery systems [2]. Mucoadhesive films offer many advantages, like prolongation of the residence time at the site of absorption, thus enhancing the absorption and hence the therapeutic efficacy of the incorporated drug. The good blood supply of the oral cavity enables a rapid absorption and avoidance of the first pass effect, thereby increasing bioavailability [3]. The aim of the present work was to study the effect of plasticizer type/quantity on the thermal behaviour of chitosan mucoadhesive films made with acetic acid (AA) and citric acid (CA). The films were prepared by solvent casting method, by dissolving 2 w/v% of chitosan-80/1000 (Heppe, Germany) in 2 v/v% aqueous AA 99.8% (Sigma-Aldrich, Germany) solution as prescribed by Liu et al [4] as a reference; and with the use of CA monohydrate (Molar Chemicals KFT, Hungary) in a quantity of 2.5, 3, 3.5, 4, 5 and 7 w/v %. Glycerol, propylene glycol and polyethylene glycol-400 were added as plasticizers to CA 2.5%, CA 7% and to AA-based solutions in an amount of 5 w/v% and 10 w/v%. A magnetic stirrer was used to obtain 100-ml homogeneous solutions. Heating to 50-58°C for two hours was required to dissolve chitosan containing a low amount of CA (2.5, and 3 w/v %), as their pH was around 4, which is higher compared to the pH of the AA-based solution (pH of ~2.75). Solutions were cast onto Teflon plates ($19.635\ cm^2$ x 0.5 cm) as 10 gram per plate, the plates were fixed at the bottom by applying a thin layer of the polymer on a smooth surface with trays to prevent any leakage and allowed to get dry under ambient condition (25.5±1°C and 28±1 RH%) for 48 hours. The dried films were carefully released from the plates and preserved in a tightly closed container for the thermal investigation. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out by using TG/DSC1 equipment (Mettler-Toledo Inc., Switzerland) coupled with Thermo Star mass spectrometer (Pfeiffer Vacuum GmbH, Germany) to analyse the evolved gases during the mass loss. The samples were heated from 25 to 500°C in a non-hermetically sealed 40 µl aluminum pan. The heating rate was $10°C.min^{-1}$. The mass of the samples was 10±2 mg, the measurements were performed in nitrogen atmosphere at a rate of $70\ ml.min^{-1}$. The role of the different plasticizers in thermal stability was examined. It was found that in all compositions the PEG-400 content increased, while the propylene glycol content decreased the thermal stability of the films. These results not only help to choose the formulation conditions but also provide useful information concerning the packaging and storage conditions as well as the stability of the final product.

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Thermal degradation of crab shell biomass

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Keywords: Chitin, thermal analysis (TG/DTG), pyrolysis GC/MS, powder X-ray diffraction (PXRD), X-Ray Photoelectron Spectroscopy (XPS)

Waste and low cost lignocellulosic biomasses are well studied and widely used as raw materials for porous carbon adsorbents. Much less attention is given to the exploration of the potential of marine biomasses, though these materials contain also nitrogen atoms which - if saved during the conversion – have a beneficial influence on the sorption behaviour of the porous carbon obtained.

Here we report a multi-technique investigation into the conversion of crab shell to porous carbon adsorbent. Thermogravimetry and pyrolysis GC/MS studies were used to reveal the thermal degradation of this natural polymer and follow the degradation process through the identification of the fragments. Almost 40 various degradation products were distinguished up to 500 °C. Based on the TG/DTG results two temperatures, 350 and 500 °C were selected to obtain pyrolytic samples in macroscopic quantities in order to characterize the developing structure and surface chemistry of the carbonaceous residue. More than 50 % of the nitrogen atoms were still in the carbonaceous matrix after the 500 °C pyrolysis as parts of C–N=C, C–NH and 3C–N bonds. The < 1 % ash content was attributed to $Ca_3(PO_4)_2$. Based on these results the carb shell is a promising raw material for biochar.

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Compositional study on key intermediate salt with high diastereomeric excess from resolution of tofisopam, by elemental, 1H-NMR spectroscopic, and evolved gas (TG-MS, TG-FTIR) analyses

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Keywords: resolution of racemic tofisopam, evolved gas analysis, TG-MS, TG-FTIR

Optical resolution[1] of racemic tofisopam, an anxiolytic agent, carried out in two-phase water/chloroform media by (*R,R*)-O,O'-dibenzoyl-tartaric acid (DBTA)[2], results in a fine yellow intermediate precipitation, which on standing in open air quickly gets a hard outer crusted layer during its natural drying process. Meanwhile, the yellow samples' wet microcrystallinity rapidly changes into stable crystalline state, which could also be monitorred by powder X-ray diffraction. This air dried sample can be considered as a key diastereomeric substance of the whole resolution process leading successfully to an enantiomerically rich (+)-tofisopam matter[2]. Exploration of composition of the yellow intermediate with high diastereomeric excess, is also thought to provide a deeper insight into the unique efficiency of this resolution process. Elemental, ^{1}H-NMR spectroscopy, and evolved gas analytical methods has been chosen to collect information on the overall composition of this so called diastereomeric intermediate sample.

The thermal behaviour of the sample has been studied in details by both TG/DTA-MS and TG-FTIR-gascell measurements at constant heating rate of 10°C/min. According to the thermogravimetric curves, a continuous and gradual weight loss (an overall 5-7% of the original air dried sample mass) is observed till 130°C. At around 130°C the rate of weight loss becomes very low, but it is increased again with the rising temperature. Actually no melting phenomenon could be detected by differential thermal analysis (DTA), indicating formation of an amorphous condensed state product, which is also confirmed by powder X-ray diffraction on a sample residues heated exactly till 130°C. Meanwhile both coupled evolved gas analyser indicated evolution of chloroform parallel to the weight changes in two steps. The evolution rate of $CHCl_3$ is fallen back actually around 130°C between the two steps, what indicates that the amorphous material also able to held some part of the chloroform captured originally in the resolution process.

The overall composition in term of molar ratios of tofisopam : DBTA : chloroform are tried to be calculated from CHN(Cl)-elemental analysis and ^{1}H-NMR-spectral data. In addition, the latter spectra reflected the varying ratio and equilibria of the two possible conformers of tofisopam usually occurring in solutions[3,4] and effect of chiral surroundings.

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Organic–inorganic transdermal therapeutic system for controlled release of Annona muricata L. for the topical treatment of rheumatic diseases

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Keywords: Annona muricata L., transdermal therapeutic systems, anti-inflammatory activity

Annona muricata L. is a tree that is part of the Annonacea family and that has been widely used by the popular medicine due to its antispasmodic, antidiarrheal, antirheumatic and anti-inflammatory properties. However, studies in the literature have shown that a high dose is required for anti-inflammatory activity. Thus, an interesting approach to decrease high doses is its incorporation into transdermal therapeutic systems (STT), developed from hybrid materials of the organic-inorganic type, which due to their chemical physical properties have high values of adhesiveness, capacity of incorporating different substances (lipophilic, hydrophilic and metal) and controlled release of drugs. Based on this principle, in this study a STT which is developed from a hybrid material called ureasil-polyether containing leaf extract of *Annona muricata* L. was developed and characterized. The cytotoxicity of the *A. muricata* extract was assessed and exhibited IC_{50} of 8.95 ± 0.21 μg/mL. Differential Thermal Analysis technique indicated that there was no incompatibility between *A. muricata* and STT. Small Angle X-Ray Scattering analysis revealed an increase in the correlation distance between the siloxane groups occurred due to the adsorption of the medium through the material that has hydrophilic characteristics. Atomic force microscopy showed that when added *A. muricata* the pores present on the surface of the ureasil-PEO material increased from 523 nm to 1.573 nm. *In vitro* release experiments revealed that the release of *A. muricata* loaded in ureasil-PEO material reached 8% release rate after 72h. The results indicate that this research offers a new alternative for the relief and control of these inflammatory pathologies with reduction or elimination of the adverse effects frequently observed with the use of conventional anti-inflammatories. Besides that, also present capacity of controlled release of the active, that could occur during days or even months, it is odorless and impermeable which prevents evaporation and oxidation of the active, also, it increases the patient's adhesion to the treatment.

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Encapsulation of antirheumatic drugs in cyclodextrin-based metal-organic framework

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Keywords: cyclodextrin, metal-organic framework, encapsulation

Metal-organic frameworks (MOFs) represent a perspective class of hybrid porous compounds having numerous applications in science and industry. Biomedical application of MOFs received a special attention in recent years due to biocompatibility and a high loading capacity of these materials. In this connection, MOFs are considered to be promising platforms for drug delivery.

In this work, metal-organic framework compounds based on γ-cyclodextrin and potassium cations (γCD-MOF) were successfully synthesized using a vapor diffusion method. Encapsulation of immunosuppressive disease-modifying antirheumatic drugs leflunomide (LEF), methotrexate (MTX) and sulfasalazine (SSZ) in γCD-MOF was performed by impregnation and co-crystallization methods. The empty and loaded γCD-MOFs were characterized using DSC, TG, X-ray powder diffraction and N2 adsorption/desorption techniques.

The mechanisms of drug adsorption were proposed. It was shown that antirheumatic drugs under study can be incorporated in porous structure of γCD-MOF in pharmaceutically relevant quantities. The influence of complex formation of γ-cyclodextrin with LEF, SSZ and MTX on the uptake capacity of γCD-MOF was considered. The impact of the molecular size, polarity and ionization state of drug molecules on the encapsulation efficiency was analyzed.

It was shown that encapsulation of drugs into γCD-MOF accelerates the dissolution process in biorelevant media and can result in bioavailability enhancement.

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Polymers

Thermal properties of polymers and the constructions performed on the 3D print base

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Keywords: thermal conductivity, specific heat, thermal expansion, polymers, mechanical properties, separated, with commas

Investigations of the thermal properties of polymeric materials are necessary for developing optimal methods and applications for treatment of these materials for examples for using for 3D printing. Knowing the thermal properties is also very important for the reason to know the strength of a construction as well as for prediction of its lifetime. The thermal properties are also important for providing solutions for possible troubleshooting during exploitation of a printed part or in a case when something needs to be changed. In this work thermal analysis was carried out using the dedicated research stand TC05 for measurement and prediction of determining the optimal process temperature during printing, comparing the quality of the treated polymeric material compared to the raw material, monitoring of effects of ageing, determining of phase separation and calculating the percentage of crystallinity. All the information were determined based on calculation off data obtained from the stand TC05 scan in form of temperature-Heat flow curve,

As the testing material there was used the ABS material (Acrylonitrile butadiene styrene) as well as the PLA polymer (Polylactic acid) in a defined temperature range. For printing of the elements three printing directions were uses as well as several variants of the internal structure of the printed bulk elements.

For investigations and analysis of the material properties beside the thermal analysis also the mechanical strength and plasticity ware measured.

As a result of the investigations a correlation between the temperature during printing, strength of the material itself as well as the printed construction and thermal properties characteristics was obtained, determining the optimal application conditions in case of thermal behaviour of the material and structural stiffness of the printed structures. Based on these investigation results this work provides useful information essential for the polymer industry as well as user of polymer based products manufactured using 3D printing.

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Melting and crystallization rates of three common feed polymers for fused deposition modelling

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Keywords: melting, crystallization, kinetics, PLA, Nylon, PVA

Fused deposition modelling (FDM) with feed thermoplastic materials is one of the most popular 3D-printing techniques. One of the advantages of this technique is its high versatility combined with a relatively low cost. A successfully print depends on multiple factors, such as layer height, raster angle, extruder temperature, printing speed, percent infill...[1,2] A wide variety of printers and feed materials are produced by many manufacturers in the world and thus, there is an enormous freedom to choose models and materials at very reasonable prices. Of course, even for the same polymer, rheological properties depend on multiple factors that may vary from one manufacturer to other. Also, features of the printer such as extruder design may seriously affect the performance of the printing process. That is the reason why some printer manufacturers recommend specific feed materials. However, there are many possible combinations of printers and feed materials that are being tried without a previous study. The present work tries to provide an approach to choose the right processing conditions based on the melting and crystallization behavior of a few feed materials that are taken as an example. Since normal operation of FDM machines involves to keep the temperatures constant at the extruder nozzle and at the deposition surface, this work is focused on the isothermal melting and crystallization of the chosen materials. Both melting and crystallization data are obtained from differential scanning calorimetry (DSC) tests and fitted to an isothermal kinetic model so predictions of melting and crystallization times at different temperatures are easily done. Studies like this could be extended to other materials in order to facilitate the setup of FDM-printing operations.

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Synthesis and micellization of nonionic dendritic polyglycerol amphiphiles

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Keywords: dendritic polyglycerol amphiphile, surfactant, micelles, fluorescent probe, ITC

In recent years, many studies on dendritic polyglycerol amphiphiles have focused on their solubilization and delivery of drug due to their low polydispersity, tunable size, good biocompatibility, and their well-defined globular self-assembled structures[1]. Although such systems might enhance performace and applications for the delivery of drug, they also exhibit some challenging issues[2]. For example, these highly defined micelles, formed by self-association of dendritic polyglycerol amphiphiles, in general contain as few as 15 molecules, indicating a severe deficiency of the alkyl chains in the hydrophobic core of the spherical micelle[3]. This behaviour is very different from the case of classical detergent micelles, in which the hydrophobic core is completely filled by alkyl chains. Therefore, the micelles formed by the dendritic polyglycerol amphiphiles are less stable and have less solubilizing ability for hydrophobic drugs. In this work, the non-ionic dendritic glycerol-based amphiphile ($C_{12}[G_3(\text{P-Glycol})OH]_2$, referred to as G_3) was synthesized, and its aggregation behaviour also was studied by fluorescent probe method and isothermal titration calorimetry (ITC). In order to improve the stability of hydrophobic cores of these micelles, we also investigated the micellization behavior of the mixtures of the dendritic amphiphilic G3 and some traditional surfactants. Futher our studies showed that these more stable mixed micelles had better solubilizing ability for hydrophobic model drugs.

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Effect of hydrogen-bond density on the crystallization kinetics of polyamides investigated by flash DSC measurement

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Keywords: Flash DSC, polyamides, hydrogen-bond density, crystallization kinetics

Polyamides (PA), commonly known as nylons, are a kind of linear polymer with repetitive sequences of sheet-like hydrogen bonds between their backbones. The different hydrogen-bond densities of of various PA have a substantial impact on their crystallization kinetics at both high and low supercooling of the melt. In the present work, we employed the commercial Mettler-Toledo Flash DSC 1 [1] to study the isothermal crystallization kinetics of polyamide 46 (PA 46), polyamide 610 (PA 610), polyamide 612 (PA 612) and polyamide 1012 (PA 1012). The results reveal that the crystallization kinetics of these PA significantly depends on the hydrogen-bond density. On the one hand, in the high temperature region, PA 46 with the highest hydrogen-bond density crystallizes the fastest while PA 1012 with the lowest density crystallizes the slowest, which can be attributed to the lower lateral surface free energy barrier for crystal nucleation [2, 3] brought about by the more hydrogen-bonding interactions. On the other hand, PA 1012 crystallizes the fastest at low temperatures, indicating the higher molecular mobility in this temperature region due to the lower glass transition temperature[2, 3]. Additionally, the close hydrogen-bond density leads to a minor difference in the crystallization rates between PA 610 and PA 612.

Acknowledgements

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Prediction of tensile modulus of polylactic acid based on its structure

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Keywords: Young’s modulus, poly(lactic-acid), crystalline structure, crystallinity, lamella thickness

The properties of the semicrystalline polymers are determined by their complex crystalline structure. According to earlier reports the tensile modulus of crystalline polymers depends predominantly on their crystallinity and lamella thickness and Pukánszky et al. [1] suggested an empirical correlation for calculation of tensile modulus from the parameters of crystalline structure. Crystallinity and lamella thickness were characterized by the enthalpy and peak temperature of crystallization respectively, which values were recorded using calorimetry. Unfortunately, this linearized equation can be used only in limited range of crystallinity. Consequently, we suggested a new form of equation which can describe the modulus from 0 to 1 of crystallinity [2].

$$E = E_a + (E_c - E_a)e^{\left(-\left(\frac{1-X}{X}\right)^{\alpha}+\left(\frac{T_m^0-T_{av}}{T_m^0}\right)^{\beta}\right)^{\gamma}}$$

E_a and E_c are the modulus of amorphous and perfectly crystalline polymer respectively, X is the crystallinity and T_{av} is the average melting temperature, which is used for characterization of lamella thickness. Both X and T_{av} can be estimated using calorimetry. The equilibrium melting temperature (T_m^0) is also needed for the calculations as well as the iterative constants of α, β and γ. These values were determined for iPP and PA6 in our recent publication [3], however they are unknown for polylactic acid (PLA). Accordingly, this work aims the adaptation of Equation to PLA, because the demand for PLA is increasing continuously nowadays and a lot of development is dealing with the potentials of this compostable polymer. Our goal is also the prediction of the potential as well as the limitations of the stiffness in PLA using our approach.

The parameters of crystalline structure were determined by calorimetry (DSC). The specimens for tensile tests were fabricated using DEMAG IntElect electronic injection molding machine. Mechanical properties are determined with standard tensile test using an Instron 5566 type tensile machine.

In order to use Equation 1 for prediction of tensile modulus a set of reference samples was prepared, with significantly different crystallinity and lamellar structure. The results indicate clearly that the larger crystallinity is accompanied with larger tensile stiffness. Equation 1 was fitted to these data points in order to estimate the iterative constants. Other data like E_a, E_c and T_m^0 were estimated following the procedure in our previous work [2, 3]. The results indicated that the prediction of tensile modulus is possible in PLA similarly to other semi-crystalline polymers, because reasonably good agreement is found between the predicted and measured modulus values.

Acknowledgments

If applicable.

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Retardant treated and untreated upholstery pur foams fire hazard assessment based on the thermal analysis and cone calorimetry results

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Keywords: PUR foam, thermal analysis, thermogravimetry, differential scanning calorimetry, cone calorimetry

The materials used in the composition of the upholstered furniture are composed of flammable organic materials which may contribute in the case of a fire to its development. In the paper, there are introduced the results of thermal and cone calorimetry analyses and fire hazard assessment for upholstery polyurethane (PUR) foams, which make up a substantial part of the upholstered furniture composition. Among the PUR foams tested belonged soft foam types as KF 5560, DEFLAMO KF 4545 - with reduced flammability, high-elastic V 4010, high-elastic VF 6020 with reduced flammability and standard N 5063. For the evaluation of PUR foams, we chose the thermal analysis method - thermogravimetry and differential scanning calorimetry, according to STN EN ISO 11358 and STN EN ISO 11357-1 and cone calorimetry method (ISO 5660). The results showed the effect of retardation on the assessment parameters. The samples with retardation treatment achieved better thermal stability than samples without retardation treatment. The lowest standard thermal stability the standard

N 5063 sample achieved. In the differential scanning calorimetry analysis, all the samples showed significant exothermic effect. As the most hazardous in terms of amount of heat released was determined the N 5063 PUR foam, which released the largest amount of heat (4,199.9 J·g-1) at temperature of 322.4 °C. In the second decomposition stage, in temperature range of 449 – 595 °C, it released heat of 3 099.2 J·g-1. The cone calorimetry results showed that from heat release rate (peak value) point of view the least fire hazardous was KF 4545 PUR foam (378.27 kW·m2), followed by KF 5560 (390.01 kW·m2), VF 6020 (417.29 kW·m2), N 5063 (417.49 kW·m2), DEFLAMO KF 4545 (390.01 kW·m2) and the most hazardous was V 4010 PUR foam (683.07 kW·m2). Those results were also confirmed by MARHE (maximum average rate of heat release) values.

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Dual-curing of an epoxy resin with dicarboxylic acids

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Keywords: dual-curing, epoxy networks, diacids, isothermal curing

Epoxy resins are widely used as adhesives, coatings, castings, electrical and electronic materials, encapsulation of semiconductor devices, matrix material for components, flame retardants and in cryogenic engineering thanks to their desirable mechanical and electrical characteristics. Epoxy resins can be cured using dicarboxylic acids. During the curing, there is a competition between two processes: The first and the most important is the condensation between the epoxy and the acid groups and the second is epoxy homopolymerization that can take place at higher temperatures.

If an excess of the epoxy resin is added to the epoxy-diacid formulation, a dual-curing system can be obtained. In the first step of the dual-curing, a stoichiometric epoxy-diacid reaction takes place at low temperature. In the second step, at higher temperatures, the homopolymerization of the epoxy excess takes place. In this way, the intermediate properties of the system can be controlled to facilitate the preparation of storable and easily handled materials after the initial curing stage. Upon application of a second stimulus, these materials obtain their ultimate properties [1].

In this work, we have studied the preparation and characterization of a new family of thermosets based on off-stoichiometric diacid-epoxy formulations in the presence of 1-methylimidazole. Tri-glycidyl para-amino phenol has been used as epoxy resin and terephthalic and isophthalic acids have been used as diacids. The curing has been analyzed isothermally at different temperatures by calorimetry, using an isoconversional method and the Šestak-Berggren equation to determine the activation energy, the frequency factor and the reaction orders [2]. Two peaks appeared during the isothermal curing, the first one associated to the reaction of the carboxylic groups of the diacids with the epoxy groups and the second one related to the homopolymerization of the epoxy groups. The thermal-mechanical properties of the partially-cured and fully-cured materials have been determined by calorimetry and dynamic mechanical analysis. The analysis of the isothermal curing by FTIR (infrared spectroscopy by Fourier transform) allowed monitoring the reacting groups during the process.

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Enhancement of the thermal and mechanical properties of 3d-printing formulations using dual-curing

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Keywords: 3D-printing, dual-curing, photopolymerization

Additive manufacturing (AM) using various processing techniques is a promising alternative to conventional manufacturing process given the unique complex structures that can be achieved by processing components layer-by-layer. Among them, masked image projection stereolithography (MIP-SL), is a processing technique based on the photopolymerization of a reactive component, usually an acrylate formulation. Components produced by MIP-SL face, however, a number of drawbacks derived from the difficulty in controlling accurately the shape while ensuring uniform mechanical properties [1]. Moreover, thermal and mechanical properties are limited by the 3D-printing process, which is usually carried out at room temperature.

In order to overcome some of these drawbacks, it is proposed to enhance and make uniform the thermal and mechanical properties of an acrylate-based 3D-printing formulation used for MIP-SL making use of the dual-curing concept [2]. In this work, this base formulation is modified with a high-Tg epoxy co-monomer and a latent cationic thermal initiator [3], and a thermal radical initiator. In a first curing stage, the radical photopolymerization of the acrylate component takes place. In a second curing stage, at higher temperatures and in the absence of UV-light, the cationic homopolymerization of the epoxy groups is triggered. The activation of the thermal latent catalyst promotes the completion of the acrylate radical polymerization. The effect of the different components on the photocuring process and the subsequent thermal treatment are examined with photoDSC, DSC and FTIR. The network structure and the thermal and mechanical properties of the intermediate and final materials have been analyzed with DSC, DMA and solubility measurements. The storage stability of the uncured and partially-cured materials is also analyzed. It is shown that the properties of the fully cured materials can be fine-tuned depending on the proportion of the epoxy component, and that better dimensional stability and uniformity in properties can be achieved. In addition, the pot-life of the prepared modified formulations is sufficient for practical use.

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Fire behaviour of a cyanate-ester/epoxy blend based carbon/flax and basalt/flax hybrid composites

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Keywords: cyanate ester, fire, epoxy, hybrid composites

Hybridization by aid of either natural or synthetic reinforcements, irrespective of their inherent material characteristics (e.g. shape, length, orientation, etc.) and compatibility issues assured through various techniques seem to capture researchers' attention continuously, as can be traced by a focused survey on literature [1-2]. Thermosetting polymer resins, especially cyanate-ester (CE), are particularly of interest due to their versatility during composite materials' manufacturing, stability and fire behaviour within certain temperature range, recyclable potential and other enhanced material performances that enable delivering low weight structural materials for aerospace and automotive industries if combined with carbon fibres (CF) [3-6]. The contribution aims to present a comprehensive perspective on fire behaviour of different stacking sequences of natural (e.g. flax fibre) and synthetic reinforcements (e.g. carbon and basalt fibres) embedded within two different thermosetting resins, namely an epoxy (DGEBF) and cyanate ester (CE) blend and a plain epoxy (DGEBF) resin, from the same manufacturer (Epikote™ - Momentive). The hybrid composite architectures were delivered as laminates obtained by deployment of a hot compression moulding technique. The synthetic reinforcements were stacked either symmetrically or asymmetrically, as the most outer and the outer/middle distributed layers, respectively. The fire behaviour (e.g. fire degradation, smoke emission and heat release) will be quantified by aid of heat release rate, effective heat of combustion, mass los rate, char residue, etc. and debated comparatively not in the favour of one resin system but hybrid composite architectures management.

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Determination of thermal and thermomechanical properties of biodegradable PLA blends for 3D additive manufacturing process

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Since its inception in the 1980s, additive manufacturing has become a technology of choice due to its ability for the rapid prototyping (RP) of complex shapes and geometry directly from Computer Aided Design (CAD). To realize its full potential though, there is still room for further development in equipment designs and materials to match the requirements of industry [1]. Fossil fuel based materials are extensively used in industrial applications, however there is increasing awareness of their adverse effects on the environment and their limited resources. Considerable attention has been focussed in the recent years to replace fossil fuel based material with eco-friendly biobased/biodegradable materials. Currently, most used biopolymer in commercial applications is polylactic acid (PLA) which is derived from renewable resources such as cornstarch and sugarcane. However, PLA suffers from a series of drawbacks like brittleness, low heat deflection temperature, poor processability, and low melt strength that can be problematic in Fused Filament Fabrication (FFF) processing. Therefore, blending PLA with other polymers with desirable properties, along with the addition of environmentally friendly plasticizers and various strategies of compatibilization can overcome these drawbacks [2].

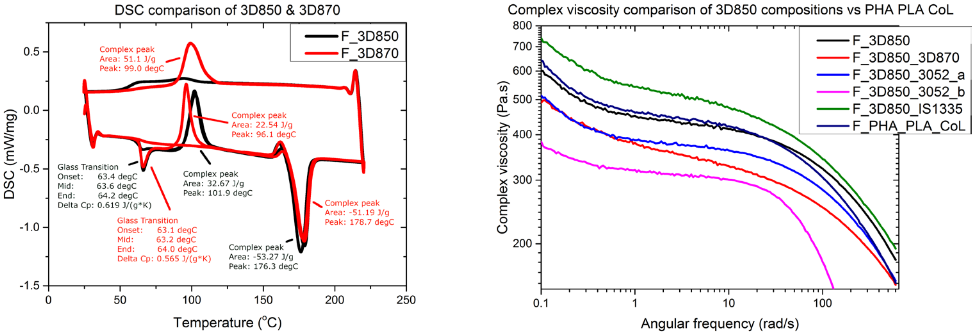

Fig. (A) Complex Viscosity vs frequency for various PLA grades (pure) and their blends, (B) Differential scanning calorimetry DSC comparison between two PLA grades.

Here, we investigated thermal and thermo-mechanical properties of different thermoplastic blends obtained from combinations of various commercially available grades of PLA and other biodegradeable synthetic polymers (Ingeo 4043D ©, Ingeo 3D850 ©, Ingeo 3D870 ©, Ingeo 3502D © from NatureWorks LLC, Ecovio IS1335 © from BASF and Bio-Flex 3D

Clear © from FKuR GmbH) using Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Rheology [3]. The properties of PLA grades and their blends are compared with the market standard material from ColorFabb BV (blend of PLA/PHA). Based on results from DSC and TGA, a lower and upper process window and thermal stability of the materials is estimated for 3D printing. The melt flow properties of the thermoplastics are studied across a range of temperatures using parallel plate rheology to investigate visco-elastic properties (complex viscosity, storage and loss modulus and tan delta) in as-received pellets from the suppliers, in filament for FFF produced via melt mixing and extrusion processing as well as in FFF specimens. We observed that the thermal and thermo-mechanical properties of filament and 3D printed part remain similar however, differences were observed for unprocessed resin to filament.

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FSC study of crystallization of cross-linked polycaprolactone

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Keywords: polycaprolactone, fast scanning calorimetry, crystallization, nucleation

Cross-linked polycaprolactone is a biocompatible and biodegradable polymeric material with high mechanical strength. Its reduced biodegradation rate in comparison with non-cross-linked polymer is prospective for encapsulation of drugs.

The physical and mechanical properties of polymers depend on the degree of crystallinity, which, in turn, is determined by the choice of thermal processing conditions. Therefore, it is of interest to study the kinetics of crystallization and nucleation depending on the degree of crosslinking. For non-crosslinked polycaprolactone, kinetics of these processes has been investigated previously [1]. However, such studies have not been performed for cross-linked polymers. We used the fast scanning calorimetry (FSC) method, which allows to heat and cool samples with a mass of no more than a few micrograms at the rates up to tens of thousands of K/s. Cooling of the polymer below the glass transition temperature at such a rate makes it possible to suppress not only crystallization, but also nucleation process.

A series of polycaprolactone samples with varying cross-link density was obtained by heating a mixture of a polymer with a radical polymerization initiator. The cross-link density was determined by the equilibrium swelling method using the Flory-Rehner equation. In FSC experiments, the sample placed onto the microchip was heated and then cooled at different rates (from 1 to 5000 K/s), then heated at 1000 K/s. With an increase in the preceding cooling rate, the total latent melting enthalpy, which is proportional to the crystallinity of polymer, decreases [2]. With an increase in the cross-link density, the crystallization rate decreases. It is shown that the magnitudes of the cooling rates leading to the half of the maximum possible crystallinity of the polymer correlate with the cross-link density values from the equilibrium swelling method.

In another series of experiments after cooling at a rate of 5000 K/s, the sample was kept for some time near and above the glass transition temperature, and kinetics of crystallization and nucleation process was studied. The curing time required for the formation of crystallization centers increases with the degree of crosslinking. The magnitude of the enthalpy of cold crystallization, observed during rapid heating, is proportional to the number of nuclei of the crystalline phase formed. The rate of nucleation was also shown to decrease with the increasing density of cross-links.

The obtained results indicate that the FSC method allows us to estimate the cross-link density of polycaprolactone samples using very small samples from the measurements of crystallization kinetics.

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Polyurethanes modified with covalently functionalized hydroxyapatite for application in bone tissue engineering

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Keywords: polyurethanes, biomaterial, hydroxyapatite

Bone tissue engineering is an efficient way to repair and regenerate damaged bone. Chitosan/hydroxyapatite-based biomaterials, cellulose and hydroxyapatite composites [1] and polylactic acid or poly(ε-caprolactone) with hydroxyapatite (HAp) [2], have been broadly studied as bone scaffolds. The amino groups of chitosan enhance cell adhesion and ensure antibacterial activity, as well as enable chemical modification of the polysaccharide with various chemical agents [3]. On the other hand, HAp can agglomerate in the polymer matrix as the intermolecular interactions between HAp and polymer chains are poor which leads to weakening of material's mechanical properties. Another approach to improve the interfacial adhesion in the polymer matrix is grafting polymer chains on the HAp surface that allow to avoid ceramics aggregation [4]. Polyurethane elastomers exhibit good mechanical and physicochemical properties, and, due to their biocompatibility can be applied in various biomedical fields [5].

In our work, poly(ethylene glycol) (PEG) with a number-average molecular weight of 2000 was grafted on the HAp nanoparticles surface using diisocyanate as a coupling agent. Next, the so functionalized HAp was introduced to polyol, and used in polyurethane synthesis with hexamethylene diisocyanate. The polyurethane prepolymer was cured with chitosan and 1,4-butanediol (BDO). The obtained nanocomposites were characterized using Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), differential scanning calorimetry (DSC), thermogravimetry (TG) and dynamic mechanical analysis (DMA).

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Applications of statistical modeling for TTS principle based on the shifting of curve derivatives

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Keywords: Time-Temperature Superposition, Statistical learning, Creep, DMTA, Rheology

The aim of this work is to introduce a new statistical model for Time-Temperature Superposition principle (TTS), and presenting its utilities through practical case study applications. The TTS principle is formulized in the framework of statistics paradigm by defining the master curve ψ (x, T). It is estimated from curves of a viscoelastic property f(x, T), defined in time/frequency domain, x = log w (with x belonging to [a, b], and w the frequency/time) and obtained at a specific temperature, T. The model is expressed as ψ(x, T) = log f(w, T) = log(bT)+ log f(log(aT)+x, T0) = B(T)+ψ(A(T)+x, T0), where A(T0) = B(T0) = 0, A(T) = log(aT) an B(T) = log(bT) are the shifts of the curves, implemented during TTS application. ψ(x, T) could be assumed as the mean of Y variable as a function of x, at a given T: ψ(x, T) = E(Y (x, T)). Accordingly, the Y variable can be expressed as a function of the master curve and a zero mean error term Y (x, T) = ψ(x, T) + ε. Where x (defined in the interval [a, b]) and T are fixed design variables, defined by the laboratory analyst. Y is the functional variable corresponding to the material viscoelastic property, ψ is the mean of Y (unknown), and ε is the error functional random variable or discrepancy between Y and ψ, not observable and in the same definition range than ψ. The first case study is concerning with the creep study of epoxy resins with applications in construction industry. For this task, DMTA tests at different temperatures have been developed. Other case studies concerning silicone modulus, PC and PS, among others, are also provided in order to illustrate the model application. The TTS package has been developed in R Software to facilitate the use of the proposed TTS model.

Acknowledgments

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Pyrolysis

Thermal behavior and kinetic study on the pyrolysis of waste engine oil

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Keywords: waste engine oil, pyrolysis, thermal behavior, kinetic parameters, diesel engine

As the world's population continuously increases, the needs for more petrol-based engines for various industries have led to huge amounts of generated waste engine oil (WEO). This organic waste can be recycled for further uses as lubricant or converted to a fuel by different methods such as thermochemical process.

In the present work, WEO is considered as an energy source to produce fuel for diesel engines. In this regard, catalytic pyrolysis process is herein used to achieve this goal. Firstly, Differential Scanning Calorimetry and Thermogravimetric experiments were conducted to determine the degradation temperatures of WEO. The activation energy and the pre-exponential factor were obtained by the KISSINGER method, by varying the heating rates (5, 10, 15 and 20 °C / min).

The physicochemical properties of the produced fuel are comparable to those of diesel fuel and in agreement with the European and American requirements. To confirm its suitability for diesel engine, an experimental study was carried out on a single cylinder diesel engine under various engine speed conditions. The results show that the combustion characteristics of the produced fuel were similar to those of conventional diesel.

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Organotin, calcium-zinc and titanium composites as reinforcing agents and its effects on the thermal stability of polyvinyl chloride

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Keywords: Polyvinyl chloride, organotin, calcium-zinc, titanium composites, reinforcing agents, thermal stability

Organotin, calcium-zinc and titanium composites were introduced to enhance the thermal properties of the poly(vinyl chloride) (PVC) materials. With the incorporation of 3.16 (wt)% TiO_2, 0.32% (wt) Sn, 0.32% (wt) Ca-Zn and 0.63(wt)% Polyol, a 1.2°C increment in the glass transition temperature and a 22.4% increase in the storage modulus were observed compared to PVC(blank). The Congo red test (195°C) showed that the initial discoloration and complete discoloration times were 70 and 93 min, respectively, while the blanks (no additives) were 5 and 7 min, respectively. Therefore the sample showed excellent thermal stability. The reduction of maximum mass loss rate was about 115% and the TG curve shifted to the high temperature region, if the heating rate is 10°C min^{-1}, and observed from thermogravimetric analysis, indicating the enhanced thermal stability of PVC composites. Moreover, the composite film is 46.5% lower than the blank at the elongation at break, and the tensile strength is increased by 2.25%. TG-FTIR analysis showed that if 0.5phr of Sn and 0.5phr of commercially available Ca-Zn was added under an argon atmosphere, which was similar to the blank, little change in the composition and peak intensity of the released gases CH_4, CO_2 and H_2O found during the pyrolysis of polyvinyl chloride. However, after adding 0.5 phr of Sn and 0.5phr of commercially available Ca-Zn and 1.0phr of dipentaerythritol, the CH_4 gas for peak intensity of the composites thermal degradation around 331.1 and 476.6°C are 114.0 and 262.0% higher than the blank, respectively. In addition the peak intensity of CO_2 is nearly unchanged and unlike the blank, there is no hydroxyl group or water formation.

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Transformations of barzas coal during its thermal treatments in carbon dioxide and hydrogen media

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Keywords: low-metamorphosed Barzas coal, thermal treatment, H/C atomic ratio, carbon dioxide and hydrogen media

Coal decomposition reactions into its smaller fragments occurring in hydrogen medium at high temperatures and pressures can be considered as an important initial step of the direct coal liquefaction (DCL) technology [1, 2]. In this work, with using a number of analytical techniques (FTIR spectroscopy, thermal analysis, elemental, component and chromatographic analyses), the temperature effects (400–550°C) on the thermal transformations of low-metamorphosed Barzas coal (sapromixite) in CO_2 and H_2 media have been investigated. Two Barzas coal modifications were chosen for thermal treatment experiments: (i) tiled coal and (ii) weathered exfoliated tiled coal ("rogozhka"). Experiments on coal thermal transformations were carried out in a laboratory mini-autoclave (of ~ 20 cm^3 volume). The autoclave with coal samples loaded was prepressured with CO_2 or H_2 to various initial pressures at a room temperature and then heated at a rate of 10–12°C/min to the temperatures ranging from 400 to 550°C and to the final pressures attaining 7.0–11.0 MPa. The duration of heating at a certain temperature was of *ca*. 20 min, after which the autoclave was cooled by a fan to ambient temperature. The following types of coal products formed in the course sapromixite thermal treatment were obtaining after these runs: 1) gaseous components; 2) resin-containing solid materials and 3) small amounts (3–5 wt.%) of liquid organic substances and/or aqueous solutions of organic compounds. The quantity of gases evolved after the autoclave cooling was controlled by a drum counter; all the solid and liquid products obtained after the reaction was finished were separating, weighing and directing to IR and chromatographic investigations, respectively. Besides that, the amounts of "coal liquids" (maltenes + asphaltenes) contained in solid phase products were measured by their sequential extraction with chemically pure *n*-hexane (to determine concentration of maltenes) and then analytically pure benzene (for separation of asphaltenes and non-extractable residues) in a Soxhlet apparatus. Almost similar extreme temperature dependencies of changes in the alkyl group ($-CH_3$ and $>CH_2$) relative IR intensities $[(D_{2920}+D_{2860})/D_{1600}]$ and the yields of "coal liquids" have been established for Barzas coal conversions in both media (CO_2 and H_2), with maximal values observed at T = 475°C. This can be explained by the initial accumulation of alkyl-containing structures and their subsequent transition into the gas phase. A pronounced relationship between the yields of gases and H/C atomic ratios in solid products of sapromixite transformations has also been discovered. It has been established that H/C atomic ratios in the solid products of thermally treated Barzas coal tended to decrease while the yields of gases formed during its hydropyrolysis, vice versa, increased. For the tiled form of sapromixite, the yield of "coal liquids" (~ 37.7 wt.%) was about 1.5 times higher, and the yield of gases (~ 10.3 wt.%) more than 2 times lower than in similar experiments with the weathered tiled modification of Barzas coal. Chromatographic analysis of organics present in an aqueous phase of the products obtained after thermal treatment of Barzas coal at 475°C suggested that the principal organic components of this phase were phenol and its methyl and dimethyl derivatives. Their total concentration in CH_2Cl_2 extract exceeded 77% by weight and 84.5% by weight for CO_2 and H_2 media, respectively. Liquid organic products were represented by mostly alcohols (predominantly 1-butanol) and C_6-C_{14} hydrocarbons.

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Pyrolysis kinetic analysis of [Bmim][DBP] through thermogravimetry and Fourier transform infrared spectrometry

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Keywords: pyrolysis process, flame-retarding mechanism, pyrolysis kinetics, kinetic function, conversion range

1-Butyl-3-methylimidazolium dibutyl phosphate ([Bmim][DBP]) has been demonstrated to be an excellent flame-retardant additive. To accurately analyze the feasibility of [Bmim][DBP] as flame retardant, pyrolysis behavior has been systematically and completely studied to investigate the flame-retarding mechanism. According to the previous experimental results, the pyrolysis process of [Bmim][DBP] investigated using nonisothermal thermogravimetry (TG) was divided into three relatively discrete stages: Moisture evaporation, bulk pyrolysis, and products pyrolysis. To research the effects of products of [Bmim][DBP] on the flame-retardant process, in this study, the third pyrolysis kinetics has been selectively analyzed. The apparent activation energy was evaluated using the AKTS–thermokinetics software to be 142.68 kJ mol^{-1} at the conversion range of 70.0%–90.0%. However, the values of E_a presented weak degree of fitting after the conversion of 90.0% because of the end of decomposition. The most probable kinetic function at the conversion range of 70.0%–90.0% appears to have an irregularity, which might be the result of a combination of multiple pyrolysis products. The residual solids derived from TG experiments were analyzed using Fourier transform infrared spectrometer, indicating that [Bmim][DBP] has typical characteristics of phosphorus flame retardant. The proposed kinetic parameters simulated pyrolysis in different conditions and thus were used for analyzing the flame-retarding mechanism of [Bmim][DBP] when applied in polymers.

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Analysis of preparation and application of ammonium polyphosphate blended with phosphorus ionic liquid

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Keywords: compounded flame retardant, thermal stability, synergistic effect, intumescent flame retardant

To optimize the flame-retardant capacity of ammonium polyphosphate (APP) and improve the flame resistance of epoxy resin materials, ionic liquid 1-butyl-3-methylimidazolium dibutyl phosphate ([Bmim][DBP]) was used as a synergist to prepare a novel compounded flame retardant with synergistic effect. In this study, the thermal decomposition processes of compounded flame retardants and modified epoxy resin composites were measured using thermogravimetry-differential scanning calorimetry. Limited oxygen index and vertical burning tests were used to estimate the flame resistance of epoxy resin composites. Results showed that [Bmim][DBP] decreased the thermal stability of ammonium polyphosphate but increased the residual mass. Furthermore, [Bmim][DBP] improved the flame-retardant capacity of APP. The limited oxygen index of epoxy resin composite modified by 10.0% compounded flame retardant reached 30.0%. However, the thermal stability of epoxy resin was decreased by the addition of APP/[Bmim][DBP], but the carbon-forming property was increased. Thus, a synergistic effect occurred between APP and [Bmim][DBP]. Especially, [Bmim][DBP] could provide carbon source, which contributed APP/[Bmim][DBP] to satisfy the condition of intumescent flame retardant.

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Theory and instrumentation

McGill Chemistry Characterization (MC^2) facility

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Keywords: facility, instruments, thermal analysis

The McGill Chemistry Characterization (MC2) facility is a multi-user facility that provides instrumentation and expertise on a wide variety of analytical and microscopy techniques. We serve both the experienced and novice investigators and our services include training for independent use, analytical services and full support from our experienced staff.

Our facilities are located in McGill's department of chemistry in Otto Maass. We serve over 100 researchers in both academia and industry.

Here we describe two of our platforms: the Microscopy and Imaging Lab (MILab) equipped with various scanning probe microscopes and electron microscope and the Thermal Analysis and Spectroscopy Lab (TASLab) with multiple DSC, TGA, UV-Vis, FTIR platforms.

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Mir imaging bundles of ordered silver halide polycrystalline fibres

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Keywords: silver halide crystals, MIR fibre bundles, thermal imaging

Silver halide polycrystalline fibres are non-toxic, non-hygroscopic, long, flexible, durable and highly transparent in the broad MIR range without absorption windows. Therefore, their arrays may be successfully used for thermal imaging applications such as intraoperative monitoring systems for laser surgery [1], biomedical diagnosis, and non-destructive inspection of various objects [2] etc. In earlier scientific papers, the development of ordered silver halide fibre bundles with common matrix has been reported [3]. In contrast with this, each of our bundles were a mechanical assembly of the fibres.

In this study, the optical characterization of two ordered bundles of polycrystalline $AgCl_{0.25}Br_{0.75}$ fibres was carried out (transmission, bandwidth, optical losses, cross-talk, and spatial resolution). The first bundle was made of 7 hexagonally arranged fibres each of diameter 300 μm. The second bundle was also made of 7 hexagonally arranged fibres, but each with a diameter of 110 μm. To the best of our knowledge, a silver halide fibre with such a small diameter has not previously been achieved.

It was found, that the bundles are transparent in the spectral range of 2.5–20 μm that corresponds to temperatures from –130 to + 900°C. The configuration used permitted low longitudinal optical losses (less than 0.5 dB/m) and low cross-talks (don't exceed 5 %), while the spatial resolution is high (the test wavelength was 10.6 μm, provided by a CO_2 laser SYNARD 48-Series-M in a continuous mode). Rather good thermal images of a heated Peltier device were taken by means of the system which included one of the two bundles, ZnSe lenses, and thermal camera FLIR E30. Moreover, the measurements of polarisation sensitivity were carried out for the larger bundle. It was revealed, that polarisation effects caused by the fibre bundle can be seen clearly.

Taking into account all the gained data, the silver halide fibre bundles have a good potential for IR thermography and can be successfully used for various applications related to this field. In the near future, we plan to develop a thermographic fibre device for medical and technical applications suitable for restricted spaces and locations where there is no line of sight between the research object and the thermal camera.

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Modeling and simulation of the operation of a calorimetric sensor for medical application

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Keywords: direct calorimetry; heat conduction calorimeters; medical calorimetry.

The purpose of the calorimetric sensor is to measure the heat flux transmitted by conduction between the human body and a thermostat located inside the sensor. The measurement surface has an area of 2 × 2 cm^2. Fig. 1 presents a schematic of the sensor. The red arrows indicate that the heat flux measured by the sensor is only that which pass across the sensor. The core of the sensor consists of a measurement thermopile (part two in Fig. 1) placed between a measuring plate (part one in Fig. 1) and thermostat (part three in Fig. 1). This thermostat consists of a small aluminium block that contains a resistance temperature detector (RTD) sensor (Pt-100) and a constantan heat resistor. To perform temperature control, there is a cooling system attached to the thermostat. The cooling system consists of another thermopile (part four in Fig. 1) and a heat sink with a fan (parts five and six, respectively, in Fig. 1). The measurement thermopile, thermostat, and cooling thermopile are thermally insulated from the outside (part seven in Fig. 1). The thermostat temperature is kept constant by a proportional-integral-derivative (PID) controller, which can maintain the programmed temperature with a resolution of ±5 mK. The model considered has four inputs and three outputs. The inputs are: the voltage applied to the cooling thermopile V_{pel} and V_{2pel}, the power dissipated in the thermostat W_{Pid}, and the power generated by the human body that passes across the sensor W_{body}. W_{body} is the value we wish to measure. The sensor is calibrated by placing it on a calibration base which generates known power signals. The outputs are: the calorimetric signal y, the thermostat temperature T_{pid}, and the temperature of the calibration base T_{base}. The model, which consists of twelve transfer functions that relate inputs and outputs, allows us to simulate the operation of the sensor. This model is useful for optimizing the measurement procedure of the sensor. This procedure consists of three phases. First, the sensor is placed on the calibration base until a steady state is reached for the set thermostat temperature. Second, the sensor is placed on the body surface where the measurement is intended to be performed. Third, the sensor is again placed on its calibration base until it returns to a steady state.

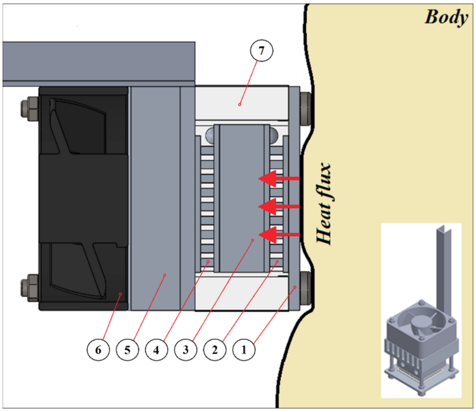

Fig. 1. Scheme of the calorimetric sensor.

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In situ Raman spectroscopy and thermogravimetric analysis: two sides of the same coin

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Symmetry, one fundamental feature used for basic characterization, determines the crystalline structure and the vibrational properties of the materials. In our recent works, we have exploited the basic correlation between interatomic distances, symmetry and thermogravimetric processes to strengthen the understanding of oxidative processes and phase transitions induced by controlled temperature increments. For example, *in situ* Raman spectroscopy have proven useful to correlate endothermic processes and mass increasing with lattice deformations at the intralayer level in black phosphorus, for the first time in literature. In another example, we correlate the decomposition of PVP thin films with the decay of all the vibrational bands in the Raman spectra. This approach offers opportunities in applications like passivation, functionalization or catalysis.

Thermal hazards, lifetime prediction

Thermal hazard evaluation of tert-butyl monoperoxymaleate by calorimetric technique

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Keywords: thermal hazard, Differential scanning calorimetry (DSC), tert-butyl monoperoxymaleate (TBPM)

Tert-butyl monoperoxymaleate (TBPM) is mainly used as organic peroxide curing agents for thermoset resins and has highly reactive and unstable exothermal features. In South Korea, due to its unstably reactive nature, TBPM has caused several thermal runaway reactions, fire and explosions accidents in the manufacturing processes. Therefore, it is important to understand its self-reactive properties, thermodynamics, and reaction kinetics for loss prevention and safety management. This study was conducted to investigate the thermal hazard of TBPM under dynamic and isothermal conditions, using differential scanning calorimetry (DSC). Exothermic onset temperature (T_o), heat of decomposition (ΔH) and activation energy (E_a) were measured and assessed. From the results, the optimal conditions were determined for avoiding violent runaway reactions in storage, transportation, and manufacturing.

DSC study of antioxidant activity of keratin hydrolysates in polyethylene glycol

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Keywords: keratin hydrolysates, polyethylene glycol, antioxidant, induction period, DSC

In this study the influence of several keratin hydrolysates on thermooxidative decomposition of polyethylene glycol (PEG) matrix have been studied by differential scanning calorimetry (DSC) under non-isothermal conditions. Thermooxidative degradation of materials exhibits an induction period, i.e. the stage where seemingly no chemical reaction takes place. The length of the induction period is frequently taken as a measure of material stability [1]. In [1,2] an integral isoconversional method is proposed for obtaining the kinetic parametres of induction periods from the onset oxidation temperatures of nonisothermal DSC runs with linear increase of temperature. Temperature dependence of the induction period can be expressed by the following equation [2]:

$$t_i = A \exp(-DT)$$

where t_i is the length of the induction period, A and D are kinetic parameters and T is the absolute temperature. For the measurements with constant heating rate, the parameters A and D can be obtained by minimizing the sum of squares between experimental oxidation onset temperatures T_i and the temperatures calculated from [2]:

$$T_i = \frac{1}{D} \ln(AD\beta+1)$$

In order to characterize the effect of individual keratin hydrolysates protection factors were calculated as a ratio of the induction periods of stabilized and non-stabilized PEG. From the values of the protection factors antioxidant effectiveness were calculated to compare the antioxidant effects of individual keratin hydrolysates. The determination of these two criteria allows reliably quantify the antioxidant effect of any additive in any matrix.

Acknowledgments

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DSC study of gamma radiation and temperature ageing of polyethylene cable insulation

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Keywords: polyethylene, ageing, thermooxidative stability, induction period, DSC, gamma radiation

Ageing of polymeric materials leads to deterioration of their physico-mechanical and chemical properties and therefore represents a serious problem, especially in the case of cable insulations in nuclear power plants [1]. Materials in these environments degrade due to several simultaneous effects, most common degrading factors are the presence of the oxygen, heat and radiation. Therefore, it is necessary to predict the thermooxidative stability of cable insulations in such conditions. Accelerated aging tests are frequently used to estimate the extent of degradation, in which radiation and elevated temperature are applied, simultaneously or separately, in quite a short time [2]. Subsequently, various diagnostic methods are applied - the most common ones are thermoanalytical methods, especially differential scanning calorimetry (DSC).

In this work, samples of medium density polyethylene (PE) cable insulation were subjected to thermal and γ-radiation stress; a combined thermal and radiation test was also performed. Stability of cable insulation was studied by DSC. Isoconversional kinetic analysis employing a non-Arrhenian temperature function was carried out [3]. The kinetic parameters enabled to calculate the length of induction period for a chosen temperature and to evaluate the residual stability of PE cable insulation after an artificial ageing stress. The results obtained in this study demonstrate that both γ-radiation and thermal ageing accelerate thermooxidative degradation of PE cable insulation. It has been shown that the decrease of residual stability with ageing dose obeys a first-order kinetics. A simple predictive model for the degradation in combined radiation and thermal environment has been proposed and verified for the samples stressed by combined ageing. Moreover, the modelling procedure presented here can also be applied to predict residual stability decrease for any given temperature and dose rate conditions.

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Thermal hazard analysis of polymerizing substances

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Keywords: thermal hazard, thermal polymerization, polymer thermal decomposition, evolved gas analysis

In the united nations recommendations on the transport of dangerous goods [1], it is described, additionally from previous revision, that polymerizing substances includes substances which, without stabilization, would be forbidden from transport due to being liable to dangerously react under conditions normally encountered in transport. These substances are easy to undergo thermal polymerization and release large amount of heat in a chemical process, for instance transport, storage, distillation, disposal and of course, reaction process. Once an unwanted initiation of polymerization occurs in transport or storage, it is especially hard to return to normal operation states. To make safety countermeasure against runaway polymerization, it is necessary to understand the whole scenarios until occurrence of the most destructive phenomena. Thermal decomposition of polymers produced during runaway polymerization is conceivable as one of the destructive phenomena. The reason for this is considerable amount of pressure release due to low molecular gasses such as CO_2, H_2O, CH_4 and NO_x evolved during the polymer thermal decomposition. Thermal decomposition of several polymers prepared in a controlled polymerization is known well in the field of macromolecule chemistry [2,3]. On the other hand, it is still unclear the polymer structure formed by spontaneous polymerization of the polymerizing substances, and the decomposition gases of them. Therefore, thermal hazard including evolved gases from polymer thermal decomposition as well as self-accelerated polymerization due to exothermal reaction is needed to be declared.

The aim of the present study is to obtain better understanding of thermal hazard of polymerizing substances. We prepared several monomers; e.g. acrylates and vinyl compounds as samples, and conducted Calvet type calorimetry using Setaram C80, accelerating rate calorimetry (ARC), and Evolved gas analysis using thermogravimetry-differential scanning calorimetry-mass spectrometry-infrared spectrometry (TG-DSC-MS-IR). Finally, we discussed about progress events during the runaway polymerization and the safety countermeasures against each event based on the above experimental results.

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Thermal hazards of 1, 1, -di-tert-butylperoxy-3, 3, 5-trimethylcyclohexane with impurities

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Keywords: 1, 1,-Di-(tert-butylperoxy)-3, 3, 5-trimethylcyclohexane (TMCH), impurity, thermal stability, runaway reaction, thermokinetic parameter

Thermal hazards of 1,1-Di-Tert-Butylperoxy-3,3,5-Trimethylcyclohexane with impurities 1,1,-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH) is widely employed as an initiator and crosslinker in rubber industry processes. The impurities that affect the thermal stability of TMCH during production and storage are water, acid, alkali, and crosslinkers. With a view to preventing unexpected runaway reactions, thermal hazard analyses of TMCH mixed with four impurities, namely water, nitric acid, sodium hydroxide, and 1, 3, 5-tri-2-propenyl-1, 3, 5-triazine-2, 4, 6 (1H, 3H, 5H)-trione (TAIC) (crosslinker) were conducted in this study using differential scanning calorimetry (DSC). All tests were conducted with four heating rates, namely 4.0, 6.0, 8.0, and 10.0 °C min–1. Thermokinetic parameters, such as exothermic onset temperature (T0), peak temperature (Tp), decomposition heat (ΔHd), and apparent activation energy (Ea) were determined. Compared with pure TMCH, the addition of water and alkali evidently increased T0 and Ea values, thereby indicating that water and alkali inhibited the decomposition of TMCH. The addition of nitric acid evidently decreased T0 of TMCH, whereas Ea shifted only not significantly, thereby indicating that the addition of acid contributed to the decomposition of TMCH. The thermal analyses of TMCH mixed with TAIC were conducted by DSC at 6.0 °C min−1. Various mass ratios (10%, 20%, 30%, and 50%) of TMCH and TAIC were analyzed. With an increase in TAIC content, Tp decreased, the peak of heat flow increased, and T0 exhibited a minor shift; these findings revealed that TAIC accelerated the decomposition of TMCH and the catalytic effect was more evident as the amount of TAIC increased.

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Evaluation of thermal reaction for AIBN and AMBN by 20-l-apparatus and calorimetry

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Keywords: azo compounds, 20-L-apparatus, synchronous thermal analyzer, differential scanning calorimetry, vent sizing package 2

Azo compounds are widely used in dyes, pigments, initiators, and blowing agents in industrial processes. Unfortunately, azo compounds inherently contain the bivalent unstable –N=N– composition, which might be readily broken during a high ambient temperature. The self-accelerating decomposition might cause a runaway reaction and lead to a fire, explosion, or leakage when the cooling system fails or other upsets occur. To explore the thermal stability parameters and explosion properties of 2,2'–azobisisobutyronitrile and 2,2'–azobis–2–methylbutyronitrile with thermal hazard and mechanism, a 20-L-apparatus, synchronous thermal analyzer, differential scanning calorimetry, and vent sizing package 2 were adopted with explosive, dynamic, and adiabatic conditions to acquire explosive curves, thermal curves, and thermodynamic parameters of the substance. Differential isoconversional method (Friedman method) was utilized to obtain the apparent activation energy. The results could be selected to construct the azo compound thermal hazard database for searching or reference example in terms of providing to industry and related research areas.

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High-pressure DSC study of coriander oil oxidative stability

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Keywords: oxygen presure, coriander oil, induction period, DSC

Oils and fats are the richest source of energy in terms of human nutrition and they also have a significant impact on the sensory quality of food. The oils are relatively prone to degradation processes because of their reactive sites in chemical structure. For this reason, their stability is an important qualitative attribute from a nutritional and sensory point of view. One of the most common degradation processes occuring in oils is thermooxidation. Thermooxidative degradation occurs in two steps. The first is induction period (IP), where seemingly no chemical reaction takes place [1]. At the end of IP the second step - oxidation itself begins. The end of IP is characterized by a rapid oxygen uptake and often a sudden change of material characteristics occurs. Therefore, the length of the IP is frequently taken as a measure of a material stability [1].

The aim of this work was to study the thermooxidative stability of coriander oil. The thermooxidation of the sample was studied employing non-isothermal DSC measurements under various pressures of oxygen. The experimental procedures were carried out in an atmosphere of air at atmospheric pressure and in an atmosphere of oxygen at atmospheric and elevated pressures using a high-pressure DSC cell at seven various heating rates. Kinetic parameters describing IP of the thermooxidation and the order of the thermooxidative degradation reaction with respect to the oxygen pressure were obtained from the dependence of the onset oxidation temperatures on the heating rate by isoconversional method using Berthelot-Hood temperature function. Their values enabled to predict the length of the isothermal IP in the temperature range from 25 to 180 °C and pressure values between 0.21 and 40 bar. It is shown that the length of the induction period decrease with increasing both temperature and partial pressure of oxygen.

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Thermal behavior of coal-field sample from Liuhuanggou, Xinjiang, China influenced by low oxygen concentration and temperature

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Keywords: temperature programmed experimental system, thermal energy release, gas emission, characteristic temperatures, thermokinetic parameters

Coal-field fires result in much loss of resource and severe harm to human-beings. To investigate the low oxygen and temperature effects on the thermal behavior of a coal-field fire, typical coal samples from Liuhuanggou, Xinjiang, China, were selected. A self-developed temperature programmed experimental system was adopted to test the thermal energy release, gas emission, and characteristic temperatures under 200 ^{o}C. The thermal behavior of this typical coal under different oxygen concentrations was revealed by the method. It showed the different oxygen concentrations (21, 15, 10, 7, and 3 vol%) had a great influence on the characteristic parameters. 10 vol% oxygen concentration was chosen as the critical concentration, which had the lowest thermal release and gas emission among the five types. Furthermore, the key thermokinetic parameters of low oxygen concentration could be obtained by thermogravimetry–differential scanning calorimetry (TG-DSC), including apparent activation energy (E_a), mass loss derivative (DTG), and reaction duration.

Thermochemistry

Sulfation performance of calcium-based sorbent in the presence of CO_2

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Keywords: Calcium carbonate, Calcium oxide, Sulfation, SO_2, CO_2

SO_2, as a main air pollutant in the world, is mainly emitted from coal-fired power plants or boilers, which has brought a serious danger for the human health and environment. Besides the utilization of clean and renewable energy, it is necessary to develop the low-cost and effective technology for reducing SO_2 emissions. Although there are large number of methods for removal of SO_2, the absorption of Ca-based material is preferred due to its low-cost and economical availability. The sulphur retention of Ca-based sorbents is influenced by temperature, CO_2 concentration, particle size and SO_2 concentration [1]. In this work, two kinds of calcium-based sorbent ($CaCO_3$ and CaO) were used as sorbents. The effect of SO_2 and CO_2 concentration on the sulfation reaction was studied by thermo-gravimetric analysis method. The ultimate conversion rates of CaO and $CaCO_3$ were 0.27 and 0.52 at the1000ppm SO_2. As the SO_2 concentration increases to 3000ppm, the conversion rate of CaO and $CaCO_3$ increase by about 23.07% and 30.15%. The final conversions of $CaCO_3$ are larger than those of CaO at SO_2 concentration of 1000, 2000 and 3000 ppm. As for CaO, the addition of 15% CO_2 makes the conversion rates increase by about 6.65% and 8.53% at the SO_2 concentration of 1000 and 2000 ppm. This work will provide a basis data for for desulphurization of Ca-based sorbents in several kinds of combustors.

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Synthesis, physico-chemical and thermal characterization of coordination compounds of Cu(II) with a pyrazole type ligand

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Keywords: copper(II), pyrazole type ligand, synthesis, structure, thermal properties

Numerous pyrazole derivatives are biologically active [1-3] or can be used as precursors for synthesis of biologically active compounds [4]. Copper is a trace element with significant biochemical role in the organism. In accordance, the aim of this work was to prepare and characterize potentially biologically active coordination compounds of Cu(II) with ethyl-5-amino-1-methyl-1H-pyrazole-4-carboxylate (L) and different co-ligands in order to examine the possibilities of a future application. In the reaction of warm methanolic solutions of CuX_2 (X = Cl, Br, NO_3) and the ligand in molar ratio 1:2, bis(ligand) complexes of the general formula $Cu(L)_2X_2$ (X = Cl, Br, NO_3) are obtained. Unlike this, the reaction of $Cu(OAc)_2$ with the ligand in the presence of LiOAc, yielded a dimeric structure of $[Cu(\mathbf{L})(OAc)_2]_2$, with four acetate ions acting as bridging ligands and direct Cu–Cu bond [2.6726(7) Å]. It should be emphasized that the latter is the first structurally characterized complex with this ligand. In all these complexes, ligand L is coordinated in a monodentate manner through N^2 nitrogen atom. The coordination environment in the dimeric complex is octahedral, while in the monomeric complexes the central atom is tetra-coordinated. The molar conductivity data in DMF shows that the acetate ions in the dimeric complex are coordinated even in solution. In the monomeric compounds, the molar conductivity data with $Cl^- > Br^- > NO_3^-$ co-ligands increase: the chloro-complex is non-electrolyte, in the bromo-complex the molar conductivity data indicates a 1:1 electrolyte, while the dissociation in the nitrate compound is practically complete in DMF.

The thermal stability of the monomeric compounds in flowing nitrogen increases in the same order as the molar conductivity data. The thermally most stable compound is $[Cu(L)_2Cl_2]$ with a DTG onset of 198 °C. The onset temperatures of the bromo- and nitrato-compounds are 167 °C and 160 °C, respectively. The DTG onset of the dimeric acetate complex is 163 °C. The course of the decomposition is different in the case of the nitrato-compound, due to the presence of nitrate ion which is a strong oxidation agent. Therefore, its decomposition starts with a very week endothermic process. The first abrupt mass loss most probably belongs to the scission of the ethyl group (Δm ~ 5, calcd: 5.5 %). The reaction turns into a relatively sharp, strongly exothermic one at around 190 °C. In the other complexes, the mass loss is continuous with more (in the dimeric complex) or less overlapped endothermic reactions to about 350 °C. Above this temperature with the oxygen atoms of the ligand relatively slow exothermic oxidation processes start. Neither decomposition is completed to 600 °C.

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Energetic and structural studies on biomass degradation compounds

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Keywords: Calorimetry, Thermodynamic Properties, Predictive Schemes

The thermochemical processes of biomass conversion are based on the conception of breaking down the biomass to smaller building block molecules from which new chemicals can be generated. Thus, accurate knowledge of thermodynamic data related with those processes is crucial in guiding experimental investigations to produce valuable products from biomass.

In this context, our research group has been involved in a systematic experimental and theoretical study on key compounds derived from biomass, namely vanillyl alcohol[1], cellulose allomorphs[2], levoglucosan[3], indanone derivatives[4] and cyclic alkenones[5].

The present work reports an experimental and computational study of thermodynamic properties of substituted/unsubstituted cyclic ketones, components of the degradation of biomass. The experimental data are determined mainly from calorimetric measurements, where the principal data analysis focuses on the standard molar enthalpy of formation, an essential thermodynamic parameter associated to the molecular energy. This thermochemical information for biomass components is relevant for the evaluation of the chemical behaviour of such species, as well as to investigate a chemical reaction or other transformations in which the compounds are involved. In parallel, the results obtained from computational approaches are used to support the development of strategies allowing the establishment of reliable prediction schemes of the corresponding properties for other related compounds.

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The use of thermal analysis to study the formation of garnet ferrite (Y0.5Bi0.5)3(Fe0.5Ga0.5)5O12

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Keywords: nanosized powders, gel combustion, single-phase garnet, thermal analysis

Interest in the synthesis of ceramics based on substituted iron-yttrium garnets (Y3Fe5O12, YIG) arises from the possibility of preparing promising materials with thermodynamically stable magneto-optical properties.

In this work, we report on the successful synthesis of bismuth and gallium co-substituted ferrite garnet using a gel combustion method with polyvinyl alcohol. We have paid the most significant attention to investigation of the synthetic steps, transformation of the precursor species to the final product.

In order to identify the thermal behavior of the gel, we applied simultaneous thermal analysis (TGA/DSC). It has been established that a multi-step mass loss occurred in the range of 25–600 °C. Initially, there was a mass loss and a corresponding endothermic effect associated with the removal of water.

In the temperature range of 80–300 °C, two endothermic effects accompanied by a significant mass were observed. These effects were due to oxidation of the organic components, accompanied by intensive gas release. Such behavior is the initiation of gel combustion. A further increase in temperature up to 600 °C resulted in a slight mass loss of 5%, which can be attributed to residual carbon oxidation. Such calm combustion of the gel in the temperature range of 200–300 °C produces a fine powdery xerogel. According to the powder XRD data, a xerogel is amorphous. Thermal treatment at 300–600 ºC also did not result in the crystallization of the samples, as demonstrated by an absence of diffraction reflexes on the corresponding p-XRD patterns. Taking the obtained data into account, we considered. The thermal behavior of xerogel after heat treatment at 500 ºC was considered in detail. In the range of 550–700 ºC, there was a mass loss of 9%, accompanied by an exothermic effect with a maximum at 697 ºC. This was probably due to the thermolysis of the polymer-salt complex and the crystallization of the final product. The powder XRD analysis confirmed that the formation of polycrystalline (Y0.5Bi0.5)3(Fe0.5Ga0.5)5O12 ferrite occurred in the range of 600–760 ºC. The position of diffraction peaks corresponded to the garnet cubic phase.

Thus, according to our research, crystallization of the (Y0.5Bi0.5)3(Fe0.5Ga0.5)5O12 powder occurred at 700 °C, without intermediate and impurity phases. The intensive release of gaseous products during the synthesis caused the formation of fine and weakly agglomerated powder with a narrow particle size distribution which did not exceed 100 nm.

The final homogeneous single-phase garnet may be regarded as a promising research object for the creation of magneto-optical ceramics.

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