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ORIGINAL PAPER



The effect of addition of low-layer graphene nanoparticles on structure and mechanical properties of polyurethane-based block copolymers

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Abstract

The effect of low-layer graphene nanoparticles (LLGNP) at concentration from 0.002 to 0.1 wt.% on physical-mechanical and structural parameters of multi-block polyurethanes based on oligodiethyleneglycol adipinate, 2,4-toluylene diisocyanate and 1,6-hexamethylene diisocyanate mixture and bifunctional chain elongation agents, 2-aminoethanol and 1,4-butanediol has been studied. Three methods for LLGNP addition in polymer were compared: (1) in a reaction mixture at the polymer synthesis on a macrodiisocyantate formation step (in situ 1 method); (2) in the polymer solution at a final reaction step (in situ 2 method); and (3) in polymer melt (ex situ). It has been shown that using of the in situ 2 method provides an increase in Young's modulus of the nanocomposites. For ex situ method, a significant increase in tensile strength of the material with growth of LLGNP concentration was detected.

Keywords Polyurethane · Low-layer graphene nanoparticles · Mechanical properties · Small-angle X-ray scattering experiments

Introduction

Recently, carbon nanomaterials are used as nanofillers for design of composite materials with physical-mechanical and operational characteristics exceeding metals and alloys [1–3]. Interest to such materials is due to their high mechanical rigidity, thermal and chemical stability, thermo- and electroconductivity,

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good electromechanical characteristics, nonlinear optical and some other unique properties [4–9]. Among nanofillers for polyurethanes (PU), special attention is focused on carbon fillers: nanotubes, graphenes and fullerenes [10–14].

In recent years, a great number of works are focused on development of polymer composites based on graphene or graphene-like low-layer graphene nanoparticles (LLGNP) [9, 10, 15–25]. These works describe methods of functionalization of graphene nanoparticles [26] and various methods for LLGNP addition into a polymer matrix. LLGNP appear to be a more promising polymer nanomodifier than carbon nanotubes (CNT) due to higher efficiency at lower cost [27]. For example, the introduction of graphene in an epoxy binder for fiberglass plastic was found to be 1–2 orders of magnitude more effective compared to CNT for enhancement of tensile and, especially, fatigue strength [28]. The addition of 0.3 wt.% of multi-walled carbon nanotubes (MWCNT) in epoxy binder shows improvement in tensile strength by 45% compared to the neat resin [29].

The presence of surface-functionalized carbon nanofillers resulted in an increase in the tensile and impact strength of the material [30]. Composite based on polybutylene succinate matrix and only 0.1 wt.% of graphene oxide (GO) with long-chain aliphatic amine exhibits a strong increase in tensile strength and Young's modulus up to 50 and 58.9%, respectively.

For addition of nanoparticles to a polymer matrix, the following methods are widely used : mixing in melt [25], in solution [17–26, 31] and in situ polymerization in the presence of nanoparticles [18–24]. However, the most suitable for industry method of mixing in melt results in aggregation of LLGNP in a polymer matrix [32]. Mixing in solution and in situ techniques provide higher nanofiller dispersity. Moreover, in situ polymerization can be applied both for cross-linked and for soluble PUs.

The analysis of publications shows typical range of graphene concentration in PU-based nanocomposites from 0.1 to 3 wt.%. Particularly, addition of 0.5-3 wt.% of graphene nanoplates (GNP) by blending in solution provides noticeable increase in glass-transition (from -18 to -12 °C) and crystallization (from 70 to 100 °C) temperatures for multi-block PUs compared to native polymer [33, 34]. The introduction of GNP by mixing in solution leads to the growth of Young's modulus by 200% (from 30 to 90 MPa), shear viscosity at 190 °C (from ~10.6 to ~16 MPa) and tensile strain at break (>600%). The authors explain revealed effects by rigidity of GNP particle and by formation of a weak three-dimensional GNP network. The introduction of LLGNP solutions in dimethylformamide and tetrahydrofuran to similar polyurethane matrix (0.1 wt.% of nanofiller) results in higher Young's modulus, strength (by 46%) and tensile strain at break (by 38%) [18]. With further growth of concentration of LLGNP, Young's modulus increases, but strength and tensile strain at break decrease. Nanomodified polyurethanes with 2 wt.% of OH-modified GNP show an increase in strength and Young's modulus by ~240 and 200%, respectively [26].

Thus, graphene-like nanoparticles, particularly LLGNPs, are effective modifiers for rigid epoxy resins and thermoplastics elastomers. However, these modifiers are at least 100 times more expensive than polymers. Therefore, the addition of few percent of such fillers to the matrix makes the product several times more expensive that limits its application in mass production.

The problem can be solved by using of ultra-small amount of carbon nanofiller. For example, it was shown by us for cross-linked polyurethane elastomer, that addition of low amount (<0.01 wt.%) of CNT by in situ polymerization essentially improves physical–mechanical parameters of the composites [35]. This approach can be extended to the other types of polymer matrices and opens wide perspectives for their practical application.

In the present work, we study the structure and mechanical properties of MBPUbased nanocomposites. Recently, there are only few publications reporting on the improvement in mechanical properties of such polymers by addition of CNP [4–8, 35]. It is well known that distribution of nanofiller plays an important role for the improvement in final properties of nanocomposite. The dispersion of nanoparticles in the polymer matrix can be controlled by the decrease in their concentration or by optimization of addition method. In this work, we address the effect of LLGNPs addition method for improvement in the mechanical characteristics of the composites with wide range of nanoparticles concentration (from $\phi \sim 0.004$ to $\phi \sim 0.1$ wt.%) to find optimal parameters for design of MBPU materials with high performance.

Experimental

Materials

Oligodiethyleneglycoladipinate diol (ODEGA) was dried at 80 °C in vacuum for 4 h prior to use. The content of OH-groups determined by a chemical method [36] was 1.7%. Diisocyanates (2,4-toluylene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HMDI)) purchased from Aldrich were distilled in vacuum at 50–55 °C/12 mm Hg and stored in sealed ampoules. The content of isocyanate groups in diisocyanates determined by a chemical method [36] was 99.9% of the theoretical value.

Chain elongation agents, namely aminoethanol (AE) and 1,4-butanediol (BD), were purified by standard procedure [37]. The content of functional groups determined by a chemical method [36] was 99.9% of the theoretical value.

Catalyst dibutyltindilaurate (DBTDL) was purchased from Aldrich and used as received.

Methylene chloride, 99.5%, for analysis, stabilized with ethanol, was purified by standard procedure [37]. However, such an approach does not allow to fully remove stabilizer (ethanol) from the solvent, and therefore we have developed a new removing procedure. For conversion of ethanol to urethane, pre-purified methylene chloride was treated by HMDI. The disappearance of OH-groups and NCO-groups, and the appearance of urethane groups were monitored by IR spectroscopy. After ethanol conversion, methylene chloride was distilled.

LLGNP with specific surface of ~ 600 m²/g were prepared by thermal reduction of graphite oxide [38]. The content of carbon determined from elemental analysis was 89.95%. The product also contains oxygen (4.2%) and hydrogen (0.73%) in

hydroxyl, epoxy and carboxyl groups. From this, the average number of graphene layers in LLGNP calculated from theoretical value of specific surface for a single graphene layer (2630 m²/g) was found to be ~4.4.

Synthesis of multi-block polyurethane thermoplastic elastomer

Multi-block polyurethane thermoplastic elastomer (MBPU) was prepared by a three-stage method from ODEGA, mixture of symmetric aliphatic HMDI and non-symmetric aromatic TDI and chain elongation agents BD and AE. The reactions were performed in methylene chloride in the presence of DBTDL in argon atmosphere at room temperature.

On the first stage, macrodiisocyanate (MDC) was synthesized from ODEGA and TDI at double excess of NCO-groups relative to OH-groups, $[NCO_{TDI}]/[OH_{ODEGA}] \approx 2$. Then, AE $([OH_{AE} + NH_{2AE}]/[NCO_{TDI}] = 1.3)$ and BD $([NCO_{TDI+HMDI}/[OH_{ODEGA}] \approx 3.9)$ were added. On the second stage, linear PU was synthesized by the reaction of ODEGA with HMDI ($[NCO_{TDI}]/[OH_{ODEGA}] \approx 1.4$). At the third stage, all reaction products were mixed, and HMDI was added to a stoichiometric ratio [NCO]/[OH] = 1.

When degree of conversion in NCO-groups attained ~98%, the product was poured out in a flat Teflon mold and dried at 40 °C for 24 h to constant weight. Then, the prepared film was removed from the mold and stored at 40 °C for 2 weeks. The degree of conversion was controlled to the full disappearance of IR absorption bands of isocyanate ($\nu_{\rm NCO} = 2271 \text{ cm}^{-1}$) and hydroxyl ($\nu_{\rm OH} = 3620 \text{ cm}^{-1}$) groups. For physical–mechanical tests, films of 0.7 mm thickness were pressed at 90–110 °C, and paddle-like samples were cut out.

Previously, it was found that physical-mechanical characteristics of prepared MBPU noticeably change upon storage at room temperature for several months [39]. Therefore, all tests for polymers and composites were performed in 4 months after preparation when characteristics were stabilized.

Addition of LLGNP in polyurethane block copolymer

The properties of polyurethane-based thermoplastic elastomers can be tuned by adding LLGNP which form additional physical network due to non-covalent interaction with the polymer matrix. Since efficiency of interaction of polymer and nanofiller is determined by distribution of nanoparticles in the bulk, method of its addition is crucial for final performance of the material. In the presented work, we compare the most technological method of addition of the nanofiller to the reaction mixture (in situ 1) with commonly used approach based on insertion of the LLGNP in solution after polymerization (in situ 2). In addition, we check perspective for industrial application technique of LLGNP addition to polymer melt during extrusion process (ex situ). Advantages and disadvantages of each approach will be discussed later.

LLGNPs were added in MBPU by three methods

Addition of LLGNP to reaction mixture at a step of macrodiisocyanate formation (in situ 1)

LLGNP suspension in methylene chloride pre-machined in 23 kHz ultrasonic bath for 20 min was added to MDC solution prepared at the first step. The reaction mixture was stirred, and chain elongation agents and diisocyanate remainder were added. Then, MBPU was synthesized using the procedure discussed above.

Insertion of LLGNP in polymer solution at a final step of synthesis (in situ 2)

LLGNP suspension in methylene chloride pre-machined in 23 kHz ultrasonic bath for 20 min was added on the third stage of synthesis after mixing of all components in the reaction solution. Then, MBPU was synthesized using the procedure discussed above.

Addition of LLGNP to polymer melt (ex situ)

Concentrated MBPU/LLGNP mixture (0.36 wt.% of LLGNP) in methylene chloride after ultrasonic dispersion for 20 min was poured out in a flat Teflon mold and dried at 40 °C for 24 h. Then, the calculated amount of prepared MBPU/ blend was co-extruded with pure MBPU using a HAAKE Minilab II doublescrew extruder with codirectional screws at 80 °C under argon atmosphere. Maximal pressure $p_{\text{max}} = 200$ atm and maximal torque $M_{\text{max}} = 5.5$ Nm provide effective dispersion of LLGNP in polymer matrix. The material was unloaded automatically from the extrusion machine to a molding cylinder with screw rotation rate 50 rpm and temperature 50 °C. Plunger pressure on a cylinder rod was 30 MPa. Non-modified MBPU was prepared in similar conditions.

In Fig. 1, schematic representation of three methods of preparation is given.

For fabrication of the nanocomposites, LLGNP were dispersed in methylchloride by ultrasonic treatment on an ultrasonic generator IL10-0.63 at tip diameter of 15 mm, power of 472 W and frequency of 23 kHz. For mechanical and relaxational experiments, uniform 0.7-mm-thick films were prepared by thermal molding at 90–100 $^{\circ}$ C

Experimental techniques

Differential scanning calorimetry (DSC) was carried out using a DSC 30 (Mettler Toledo) calorimeter operating in a dynamic mode. The dynamic scans were performed at the heating/cooling rate of 5 °C/min under nitrogen atmosphere. Sample mass was 10.0 ± 0.2 mg. Thermal parameters were calculated from the first and second heating scans. Glass-transition temperatures (T_g) of the samples were



Fig. 1 Diagram for the preparation of LLGNP/MBPU composites by in situ 1 (1), in situ 2 (2) and ex situ (3) techniques

defined as the inflection point on the curves of the heat-capacity changes and the melting temperatures (T_m) as endothermic peak onset.

Tensile tests were performed at room temperature on a Zwick TC-FR010TH tensile-testing machine at the drawing rate of 100 mm/min. Stress relaxation was studied for the films at the constant strain 300% for 200 s. Time dependence of strain was described by multi-modal Newton approach according to Eq. (1):

$$\sigma(t)/\sigma(0) = \sum_{i} A_{i} e^{-t/\tau_{i}}$$
(1)

where A_i and τ_i are weight and relaxation time of *i*th mode, respectively. Creep process of the films was analyzed on the films after stretching to 300% at constant stress of 10 MPa for 100 s.

Number (M_n) and mass (M_w) average molar masses, and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) using a Waters GPCV 2000 chromatograph equipped with refractometric and viscosimetric detectors, and a Wyatt DAWN Heleos-II light scattering detector. Tetrahydrofuran (THF) was used as an eluent (flow=1 cm³/min). The molar mass was calibrated with polystyrene standards.

Small-angle X-ray scattering experiments were performed on a Xenocs diffractometer equipped with a GeniX3D ($\lambda = 1.54$ Å) generator able to form a beam



-(-RO-CONHR₁₍₂₎NHCO-OC₄H₈O-CONHR₂₍₁₎NHCO-NHC₂H₄O-CONHR₁₍₂₎NHCO-O-)_m-

Scheme 1 Synthesis of multi-block polyurethane thermoplastic elastomer

 Table 1
 Molecular-mass parameters of MBPU depending on concentration and insertion method for LLGNP

No.	Insertion method	φ (wt.%)	GPC				
			$\overline{M_{\rm n}({\rm g/mol})}$	$M_{\rm w}$ (g/mol)	$M_{\rm w}/M_{\rm n}$		
1		0	30×10^{3}	81×10^{3}	2.7		
2	in situ 1	0.004	28×10^{3}	76×10^{3}	2.7		
3		0.008	33×10^{3}	76×10^{3}	2.3		
4		0.1	27×10^{3}	64×10^{3}	2.4		
5	in situ 2	0.004	28×10^{3}	95×10^{3}	2.5		
6		0.008	29×10^{3}	95×10^{3}	2.3		
7	ex situ	0	30×10^{3}	90×10^{3}	2.2		
8		0.002	31×10^{3}	75×10^{3}	1.9		
9		0.004	32×10^{3}	83×10^{3}	2.2		
10		0.008	33×10^{3}	81×10^{3}	2.3		

 $300 \times 300 \ \mu\text{m}$ in size. Two-dimensional diffraction patterns were measured with a Pilatus 300 k detector, which was 2.5 m far from the sample. Wave vector modulus *s* (*s*=2 sin Θ/λ , where Θ is Bragg angle) was calibrated using seven diffraction orders from fresh collagen fibers taken from rat tail. The analysis of experimental two-dimensional diffraction patterns was performed using Igor Pro Program package (Wavemetrics Inc.).

Electron micrographs of fracture surface were measured using a Zeiss LEO SUPRA 25 scanning electron microscope (SEM) (Germany) at 4 kV accelerating voltage after vacuum deposition of the conducting carbon layer.

Results and discussion

A general scheme for synthesis of MBPU can be presented as follows (Scheme 1):

Analysis of final polymers by gel permeation chromatography (GPC) reveals the effect of nanofiller addition method on molecular weight (Table 1). As one can see from Table 1, the addition of LLGNP to the reaction mixture at a step of



Fig. 2 DSC diagrams for native MBPU (1) and nanocomposites with of 0.004 (2), 0.008 (3), 0.1 (4) wt.% of LLCNP added by the in situ 1 method. Heating rate is 5 °C/min

No.	Addition method	φ (wt.%)	T_{onset} (°C)	$T_{\rm m}(^{\circ}{\rm C})$	$-\Delta H_{\rm m}({\rm J/g})$	$T_{\rm c}(^{\circ}{\rm C})$	$\Delta H_{\rm c}({\rm J/g})$	$T_{\rm g}(^{\rm o}{\rm C})$
1	·	0	44.1	51.2	39.6	_	_	- 53.5
2	in situ 1	0.004	44.6	52.9	39.0	-	-	-54.0
3		0.008	44.9	51.8	43.7	-	-	- 53.9
4		0.1	41.6	54.5	28.6	-	-	-58.6
5	in situ 2	0.004	44.9	53.2	24.5	_	-	- 54.5
6		0.008	44.2	53.6	37.8	_	-	-53.0
7	ex situ	0	43.8	51.5	41.8	2.4	26.6	-
8		0.002	43.4	51.5	40.1	-3.9	21.1	-
9		0.004	44.2	52.6	38.9	-5.0	12.9	-

Table 2 Temperature characteristics of the composites

macrodiisocyanate formation (in situ 1) slightly increases M_n and M_w , while the addition of LLGNP at a final step of synthesis (in situ 2) provides a noticeable increase in M_w of a composite. Such a phenomenon can be explained by additional elongation of long copolymer chains due to the interaction of residual functional groups with carboxyl, epoxy and hydroxyl entities of LLGNP. The MBPU samples prepared by extrusion show noticeable increase in M_n for pure polymer and certain decrease after addition of LLGNP.

Polymer chains of synthesized MBPU contain flexible ODEGA (–ORO–) fragments which are highly crystalline at room temperature. Rigid blocks are built from butanediol (– OC_4H_8O –) and urethaneurea-containing aminoethanol (– NHC_2H_4O –) residues and provide formation of relatively strong physical

network in polymer matrix. The effect of nanofiller presence on crystal phase structure was studied by DSC (Fig. 2, Table 2).

On the DSC curves, one can see endothermic peaks above 50 °C corresponding to melting of ODEGA crystalline phase. Presence of the LLGNP in the nanocomposite in concentration up to 0.01 wt.% does not affect significantly the thermal behavior. However, the increase in concentration of LLGNP to 0.1 wt.% (in situ 1 method) reveals lower glass-transition temperature and melting enthalpy and higher melting point of ODEGA (see Table 2).

The effect of nanoparticles on melting point of crystallizable block is probably attributed to the enhancement of chain mobility and formation of larger crystals of the soft block. The change in crystalline phase was proved by small-angle X-ray scattering (SAXS). The SAXS profiles (Fig. 3) of the native polymer and the composites prepared by different methods show a well-pronounced peak corresponding to long period of PDEGA crystal packing. For native MBPU, the position of maximum corresponds to the long period of 17.7 nm. For the composites, structural changes were found to depend on preparation method. Particularly, the samples prepared by the in situ 1 method show a noticeable decrease in the long period to 16.9 nm. In contrast, the addition of LLGNP at a final step of synthesis (the in situ 2 method) does not effect on the long period (17.9 nm). The extrusion process drastically changes final supramolecular structure of the material. Diffractograms of the samples prepared by extrusion show the larger slope of the linear part at small angles that could be an evidence of the large aggregates formation [40]. The intensity of small-angle maximum decreases because of the disordering of the crystal stacks under mechanical stress. In addition, for the composites prepared by ex situ method the long period increases to 18.5 nm, whereas for non-filled MBPU, the long period value remains almost unchanged. We suppose that LLGNP lamellae play a role of plasticizer and provide higher mobility for polymer chains during



Fig. 3 One-dimensional small-angle diffractograms for native polymer (curves 1, 4) and composite with 0.008 wt.% of LLGNP (curves 2, 3 and 5) prepared by the in situ 1 (curves 1,2), the in situ 2 (curve 3) and the ex situ (curves 4, 5) methods

extrusion. In the result of better ODEGA chains orientation along mechanical stress, the thicker crystals can be formed upon cooling.

Figure 4 shows electron micrographs of fractured surfaces of MBPU samples crystals. One can see significant growth of surface roughness of nanocomposite with 0.004 wt.% of LLGNP. Such changes are explained by decrease in polymer elasticity during break in the presence of nanofiller. Thus, the experimental data indicate that the insertion of LLGNP in polymer at concentration ≤ 0.01 wt.% can noticeably affect structure and properties of MBPU. The variation of supramolecular morphology and matrix elasticity are responsible for mechanical characteristics of the materials.

The analysis of physical-mechanical parameters of native and nanomodified MBPU shows that synthesized samples form a «neck» upon drawing after reaching the limit of forced elasticity, over the whole deformed region of a sample at very small increase in stress up to elongation about 400%. Stress grows up to sample fracture with further drawing. After unloading, the length of a deformed region rapidly restores to the elongation value before beginning of strain rise (~400%), and remains unchanged for a long time at room temperature (Fig. 5). The polymer transits to high-elasticity state after heating above melting point of a crystalline phase of OGEGA with restoring of initial size (residual deformation $\leq 20\%$). Thus, the studied materials show a well-pronounced shape memory effect.

Stress–strain diagrams presented in Fig. 5 show differences in behavior of native MBPU (Fig. 5, curve 1) and nanocomposite containing 0.008 wt.% of LLGNP prepared by in situ 2 (Fig. 5, curve 2) and in situ 1 methods (Fig. 5, curve 3).

In Fig. 6, one can see dependences of mechanical parameters as a function of LLGNP content and preparation method. The parameters are normalized on



Fig. 4 SEM images of the MBPU samples: native polymer in situ 1 method (a); 0.008 wt.% in situ 2 method (b); 0.008 wt.% ex situ method (c); 0.008 wt.% in situ 1 method (d)



Fig. 5 Stress–strain curves for native MBPU (1) and composite with 0.008 wt.% of LLGNP inserted in a polymer matrix by in situ 2 (2) and in situ 1 (3) methods



Fig. 6 Relative changes in mechanical properties of MBPU/LLGNP nanocomposites as a function of LLGNP content: strength (a), Young's modulus (b) and elongation at break (c)

corresponding values for native polymer: strength 43 MPa, Young's modulus 330 MPa and elongation at break 833%.

Addition of up to 0.01 wt.% of LLGNP to MBPU by the in situ 1 method provides essentially higher value of elongation at break (Fig. 6). At the same time, the strength and Young's modulus of the films stay the same. The sample with 0.1 wt.% of LLGNP prepared by the in situ 1 method reveals strong decrease in ultimate strain and tensile strength.

For the samples prepared by in situ 2 method Young's modulus grows, but strength and ultimate strain remain almost unchanged with increasing of LLGNP concentration.

It should be noted that extrusion of native MBPU provides an increase in Young's modulus from ~ 330 to 400 MPa, slight increase in elongation at break on 42% and inessential decrease in strength on 5% due to additional arrangement of polymer blocks during extrusion. The addition of LLGNP to MBPU melt slightly increases



Fig. 7 Relative change in strain with time for the sample prepared by in situ (a) and ex situ (b) methods. The calculated values are presented in Table 3

Table 3 Results of stress relaxation analysis of nanocomposites	No.	Insertion method	φ (wt.%)	Relative change in strain (%)	τ_1 (s)	$\tau_2(s)$
	1		0	53	0.84	76.8
	2	in situ 1	0.004	33	1.26	42.6
	3		0.1	176	2.21	35.45
	4	in situ 2	0.004	104	2.08	35.76
	5		0.008	80	1.71	39.29
	6	ex situ	0	65	3.54	58.86
	7		0.002	62	1.14	52.38
	8		0.004	51	1.21	51.69

tensile strength of nanocomposite. Thus, properties of MBPU drastically depend both on concentration and on method of addition of LLGNP.

Relaxation processes play an important role in the formation of mechanical properties [40–44]. In the present work, long-term mechanical behavior of the nanocomposite films depending on nanoparticles content and addition method was studied by relaxation of stress and creep experiments.

In Fig. 7, relative variation of sample strain with time at constant stress (creep) is shown. One can see that the highest value of creep was found for the nanocomposite with the highest LLGNP content (Table 3). This proves that nanoparticles work as plasticizer for polymer matrix and enhance mechanical relaxation. Samples prepared by in situ 2 method show stronger creep effect probably due to better distribution of LLGNP in the matrix. For ultra-low LLGNP concentrations, small decrease in creep with growth of the content was detected.

Relative change in mechanical stress with time reveals the decrease in final value for nanocomposite prepared by in situ 1 and in situ 2 compared to native



Fig.8 Relative change in stress after deformation to 300% with time for samples prepared by in situ method

polymer (Fig. 8). The effect of LLGNP concentration and addition method does not show straightforward tendency. For detailed analysis of relaxation process, the experimental curves were fitted with Eq. (1) according to Newton multi-mode approach. Variation of fitting parameters reveals that for all studied samples, relaxation process can be described by two modes with characteristic relaxation times τ_1 and τ_2 . Calculated values are presented in Table 3.

According to Table 3, relaxation of stress can be divided by fast (1-2 s) and slow (50–70 s) processes. The first process is probably attributed to relaxation in rigid block stabilized by hydrogen bonds. Characteristic time τ_1 gradually increases with LLGNP content for the films prepared by in situ 1 method and stays almost constant for the samples prepared by in situ 2. We expect that such behavior is related to phase separation of rigid and soft blocks. The slow process is probably responsible for relaxation in soft block, particularly for stress-induced crystallization of ODEGA. Characteristic times τ_2 for all nanocomposites prepared by both in situ 1 and situ 2 are close (35–42 s) which is significantly smaller than the value of native polymer (76 s). Thus, plasticizing of LLGNP is more affected on the soft block. Difference in slow relaxation times for native polymer and nanocomposites can be explained by faster crystallization of ODEGA block in the presence of nanofiller. For the films prepared by ex situ technique, one can see that extrusion results in increasing of τ_1 for unfilled polymer, probably due to pre-arrangement of crystalline lamellae. Addition of LLGNP decreases relaxation time of crystalline domains, but relaxation of amorphous phase (τ_2) does not depend on the presence of the nanofiller.

Thus, our preliminary experiments have shown that the introduction of ultrasmall concentrations of LLGNP as a nanomodifier significantly influence on the supramolecular structure of the polymer and on its physical–mechanical and relaxation properties.

It can be supposed that even small concentration of nanoparticles in combination with optimal method of their addition to the polymer prevents aggregation of nanoparticles. The effect of improvement in polymers characteristics can be achieved with much smaller content of expensive nanoparticles which is important for mass production of the nanocomposites.

Conclusions

The effect of LLGNP concentration and method of its addition on structure and physical-mechanical characteristics of polyurethane-based thermoplastic elastomers have been studied. It was shown that non-covalent interaction of LLGNP with polymer matrix significantly changes thermal and mechanical properties of the nano-composites. Choice of optimal concentration of the nanomodifier and of the addition method allows improving LLGNP distribution and selectively modifying composite characteristics.

It has been found by DSC and SAXS techniques that supramolecular structure of the material is strongly affected by polymer treatment. Partial lamellar stacks disordering under mechanic field during extrusion was detected. In contrast, the presence of LLGNP results in growth of melting temperature of the soft block crystals. It has been supposed that LLGNP perform as plasticizer under extrusion. As a result, polyester (ODEGA) chains are oriented more effectively and provide the formation of thicker crystals upon cooling.

The analysis of experimental data shows that the addition of less than 0.01 wt.% of LLGNP can significantly improve structure and properties of the MBPU. Changes in characteristics depend on LLGNP addition method. For improvement in Young's modulus of polymer, the most efficient was addition of modifier to polymer solution at the final step of synthesis (in situ 2). The method of LLGNP mixing with prepared polymer in melt followed by extrusion of a composite was found to be efficient for tensile strange characteristics. The method in situ 1 (the addition of modifier in solution of reacting compounds) allows increasing elongation at break.

Experiments on relaxation of mechanical stress and creep prove the role of the nanofiller as plasticizer of polymer matrix. Relaxation of stress can be described by two processes: Fast relaxation probably attributed to reorganization of rigid phase and slow relaxation of soft polyester blocks. Significant decrease in slow relaxation time after addition of LLGNP can be explained by enhanced mobility of ODEGA fragments and faster formation of crystal phase.

The proposed approach in fabrication of new MBPUs based on optimization of nanoparticle concentration coupled with addition method can open new perspectives for design of films and fibers with good mechanical performance and shape memory effect. Acknowledgements The authors acknowledge the Ministry of Science and High Education of the Russian Federation for financial support (contract No. 14.578.21.0190 (RFMEFI57816X0190)). The work was done on the theme of the state task, № 01201361836. The authors thank for the measurements in the Center for Collective Use ICPC RAS E.E. Al'yanova (DSC), V.A. Lesnichaya (Physical–mechanical), E.O. Perepelithsina (Chromatography) and N.N. Dremova (SEM).

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