

ADVANCED PHTHALONITRILE RESINS FOR OUT-OF-AUTOCLAVE COMPOSITE MANUFACTURING

B.A. Bulgakov, A.V. Babkin, E.S. Afanasieva, A.V. Kepman

Lomonosov Moscow State University, Moscow, Russia
Institute of New Carbon Materials and Technologies JSC, Moscow, Russia

Introduction

Modern aircrafts consist of carbon fiber reinforced plastics up to 50 % mass for civil ones and 70 % for fighters. Nowadays the most common matrices are epoxy and BMI resins with upper limit of operating temperatures up to 250 °C. Development of polymer matrices stable at temperatures up to 450 °C would allow replacement of aluminum alloys by CFRP in parts operating at elevated temperatures. For aerospace industries jet engine compressor blades or supersonic aircraft body parts could be of the greatest interest in terms of application of such materials. CFRP operating temperatures are determined by thermal stability of the polymer matrix. Thermosets derived from phthalonitrile resins cured in the presence of aromatic amines are known as the most heat-resistant polymers demonstrating stability up to 500 °C. The main disadvantage of these resins was poor processability due to high melting points of uncured phthalonitrile monomers (170–200 °C) which resulted in high processing temperatures during CFRP manufacturing. This set up special requirements for auxiliary materials, and quick gelation occurring at temperatures >200 °C limited sizes and shapes of the produced items.

The development of low-melting siloxane- and phosphate-bridged phthalonitrile monomers [1-3] allowed to obtain phthalonitrile resins suitable for cost-effective injection methods for composite manufacturing [4, 5]. The reported composites demonstrated moderate mechanical properties which retained at 300 °C. In the current report we describe resin formulations based on the aforementioned monomers and CFRP manufacturing with detailed characterization of the obtained materials.

Synthesis and curing

Development of the new low-melting phthalonitrile formulation became possible after synthesis of the new phosphorus-containing monomers using a two-step scheme (Figure 1). First, nucleophilic substitution reaction between 4-nitrophthalonitrile and diphenol (resor-

cinol or hydroquinone) was performed as it described in [6] resulting in formation of semi-products 1 and 2 from resorcinol and hydroquinone respectively. The next step was the reaction between 1 or 2 and phosphorus or phosphonic acid dichlorides in the presence of pyridine with formation of the target phthalonitrile monomers 3m, 4m from 1 and 3p, 4p from 2 with high yields close to quantitative. Purification of all the monomers 3-4 by washing with brine allowed to obtain 92–95 % desired product content. To obtain high-purity monomers column chromatography on SiO₂ was applied with DCM:MeOH (20:1) as eluent.

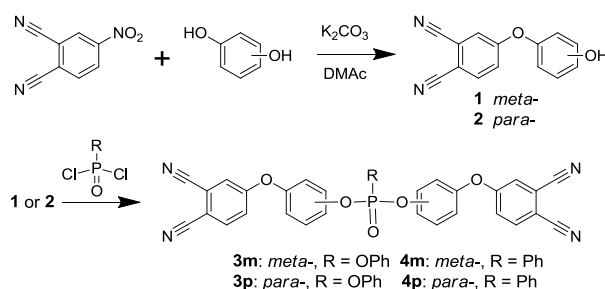


Figure 1: Synthesis of the monomers 2m and 2p.

All the synthesized monomers were yellowish glassy substances and were studied by DSC to determine glass transition temperatures. Phosphoric acid derivatives 3m and 3p possess lower T_g 's (22 °C and 42 °C respectively) than the respective phosphonic acid derivatives 4m and 4p (49 °C and 46 °C respectively). Also *meta*-substituted diphthalonitriles 3m and 4m demonstrated lower T_g 's than respective *para*-substituted ones. Monomer 3m demonstrated the lowest T_g among the synthesized phosphorus-containing monomers and thus was chosen for further experiments.

Monomer 3m was cured in the presence of 4 mol. % of 4,4'-(1,3-Phenylenedioxy)dianiline (APB) with the final temperature step of 375 °C for 8 hours. The black solid polymer obtained after curing was investigated by TMA (3 point bending) and TGA. The results are presented in Table 1. Cured monomer 3m possessed thermal properties at the same level as the common phtha-

lonitrile monomer 1,3-bis (3,4-dicyanophenoxy)benzene (5) described earlier [7] and cured in the same conditions as 3m [8].

Monomer	Thermoset properties			
	HDT, °C	T _{5%} , °C	Y _c , Ar, %	Ref.
3m	455	524	80	Here
5	441	523	75	[8]

Table 1: Thermal properties of the monomers 3m and 5 used for resin PNT formulation.

It is notable that the cured matrix obtained from 3m monomer demonstrated increased thermo-oxidative stability in comparison to cured monomer 5. This effect could be explained by the presence of a phosphate group in the molecular structure of 3m. In the experimental conditions TGA the sample of cured 3m retained almost 30 % of the initial mass at 1000 °C in contrast to the sample of cured 5 which totally combusted at 800 °C.

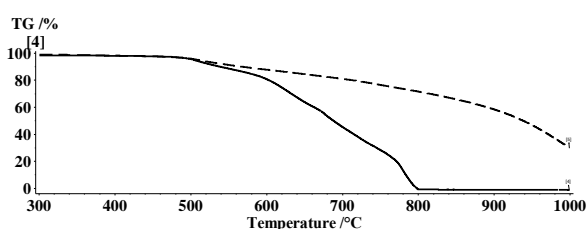


Figure 2: TGA curves of the cured monomers 3m (dashes) and 5 (solid) in air.

Resin formulation properties

Using monomers 3m and 5 in combination with diamine APB as curing agent, a formulation named PNT was developed based on rheological behavior. Blended resin PNT demonstrated melt viscosity 1000 mPa·s at 100 °C with plateau at temperatures higher than 150 °C with viscosity value 10 mPa·s (Figure 3). Isothermal experiments showed good processing time for at 120 °C sufficient for CFRP manufacturing (>24 hours) and quick gelation at 180–200 °C (30–60 min). Such properties allow to consider resin PNT for CFRP manufacturing by cost-effective injection techniques such as VIMP or RTM.

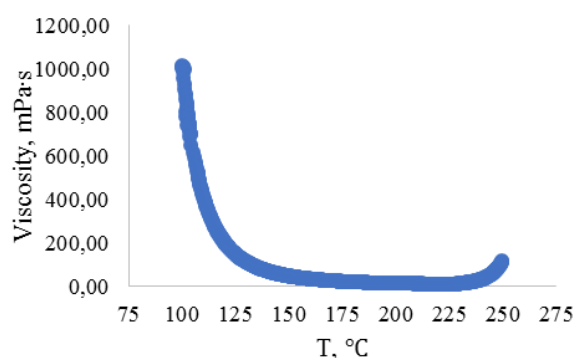


Figure 3: Viscosity profile of PNT.

Curing of PNT was performed with a two-step heating program. Based on the isothermal viscosity curves the first step was curing at 180 °C with HDT determination by TMA in penetration mode after certain time periods. Temperature of 180 °C was chosen due to respectively quick gelation of the resin at this temperature and possibility of using standard auxiliary materials such as polymeric films and sealing tape for vacuum infusion processing. It was revealed that after 3 hours at 180 °C the resin demonstrated HDT = 167 °C (determined by TMA) and 198 °C after 6 hours. Thus, the latter conditions were picked for the first step of curing because HDT higher than curing temperature was reached. The second step was heating up to 330–375 °C with heating rate 10 °C/h and holding the temperature at final step for 8 hours.

Cured resin laminates were obtained to estimate mechanical properties of the matrix. The results are presented in Table 2. It is seen that mechanical properties of the matrix post-cured at 375 °C are significantly lower than for post-cured at 330 °C which can be explained by the shrinkage causing strong inner stress in the thermoset. At the same time post-curing increases Young's modulus of the thermosets and it is important to note that the key point in this case is that the full-cycle cured matrix retained high Young's modulus at increased temperatures. No phase transition was detected on the DMA curve for the sample post-cured at 375 °C. Storage modulus of this thermoset $E' = 1$ GPa retained even at 450 °C indicating a possibility of CFRP maintenance at this temperature. One of the important properties for high-temperature materials is a low coefficient of thermal expansion (CTE): post-cured samples demonstrated $CTE = 39\text{--}63 \cdot 10^{-6} \text{ K}^{-1}$.

Parameter	Curing conditions		
	6 h, 180 °C	8 h, 330 °C	8 h, 375 °C
T _g , °C	182	320	>450
Tensile strength, MPa	59	43	–
Tensile modulus, GPa	4.2	4.8	–
Flexural strength, MPa	104	95	55
Flexural modulus, GPa	4.6	5.1	4.9
CTE, 10 ⁻⁶ K ⁻¹	63	50	39
Density, g/cm ³	1.316	1.324	1.386

Table 2: Thermal properties of thermosets derived from PNT.

CFRP manufacturing and characterization

Impregnation was performed in a programmable oven equipped with outlets for a vacuum pump at 120 °C and took about 30 minutes. After the resin appeared in outlet tube outside the oven it was sealed and heated for 6 hours at 180 °C. The sample was disassembled and post-cured at 330–375 °C resulting in heat-resistant CFRP formation with the matrix content of 30–32 %.

Mechanical characteristics of CFRP are shown in Table 3. It is seen, that curing at 330°C results in composite possessing higher mechanical properties than the one cured at 375 °C. The reason of this phenomenon is high shrinkage after curing at 375 °C which causes cracks formation in the composite (observed by SEM).

Parameter		Test method	Post-curing conditions	
			8 h, 330 °C	8 h, 375 °C
Tensile strength	σ_{11}^+ , MPa	ASTM D3039	834	685
	E, GPa	ASTM D3039	60	61
Compressive strength	σ_{11}^- , MPa	ASTM D6641	744	538
	E, GPa	ASTM D3039	61	55
Interlaminar shear strength	τ_{13} , MPa	ASTM D2344	44	36
In plane shear strength	τ_{12} , MPa	D3579	106	75
	E, GPa	D3579	6.0	5.7

Table 3: Mechanical properties of the composites.

Both obtained CFRP samples were tested for interlaminar shear strength at elevated temperatures up to 450 °C (Table 4). At 450 °C an observed shear strength was

$\tau_{13} = 33$ MPa, demonstrating retention of mechanical properties 90% of the value at room temperature.

T, °C	Post-curing conditions			
	8 h, 330 °C		8 h, 375 °C	
	τ_{13} , MPa	τ_{12} , MPa	τ_{13} , MPa	τ_{12} , MPa
300	42	89	43	75
350	–	–	41	69
400	–	–	38	68

Table 4: Mechanical properties of the composites.

Inflammability tests

Samples of the cured matrix and CFRP were tested for LOI according to the Russian standard GOST- 21793-76. Both materials showed high LOI values in comparison to the known materials. For matrix LOI was 61% and for CFRP – 79% which is highest values among the reported for any plastics.

Conclusions

Synthesis of the new phosphorus-containing phthalonitrile monomers allowed to obtain low-melting resin formulation PNT perfectly suitable for cost-effective injection methods of CFRP manufacturing. Cured resin PNT demonstrated attractive mechanical and thermal properties that allowed considering it as matrix for high-temperature CFRP. Due to epoxy-like processing, it was possible to develop convenient method of CFRP formation by vacuum infusion molding process. Composites demonstrated high mechanical properties retained for 90 % at 450 °C and exceptional fire retardant properties. Therefore, the reported CFRP could substitute aluminum alloys or titanium in the parts of aircrafts subjected to high temperatures, space ships and other fields of industry.

Acknowledgment

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Contact

Dr. Boris Bulgakov.

Lomonosov Moscow State University

Institute of New Carbon Materials and Technologies
JSC

Leninskie gory 1-11.

119991 Moscow

Russia

bbulgakov@gmail.com

www.itecma.ru