ADVANCED PHTHALONITRILE RESIN SYSTEMS FOR VACUUM PROCESSING

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ABSTRACT

Advanced phthalonitrile resin systems based on recently introduced low-melting phosphorus-containing monomers were developed. A new class of bis-benzonitirle reactive plastisizers allowed to obtain resin systems possessing improved processability (melt viscosity < 100 mPa·s at temperatures down to 120 °C) suitable for manufacturing composites by vacuum infusion molding process or RTM at the lowest reported processing temperature of 120 °C on carbon fabric (3K HTA40, twill). The curing cycle was adjusted to achieve the best mechanical properties of the composites reaching 852 MPa in compressive strength. The influence of post-curing conditions on the resulting composites properties was established. After post-curing at 375 °C the obtained composites demonstrated up to 90% mechanical properties retention at 400 °C (τ_{12} = 60-80 MPa). Solvent-free phthalonitrile prepregs were developed for the first time. Prepreg consolidation yielded high-quality composites. Flame retardant properties of investigated composites demonstrated extremely high LOI > 80%. Thus easy-processable phthalonitriles for out-of-autoclave manufacturing techniques with convenient curing conditions and excellent heat resistant and flame-retardant properties were developed.

1. INTRODUCTION

Fiber reinforced plastics (FRP) gradually replace common materials such as metals and alloys in aerospace industries. Modern aircrafts consist of polymer composites for more than 50% and more new materials and techniques are developing to take their place in the industry. Contemporary trends in composites manufacturing are aimed to use cost-effective resin injection methods instead of autoclave processing. Thus, in emergent Russian aircraft MS-21 wingbox is constructed from 25 meters long single CFRP parts produced by vacuum infusion. The most demanded technology for automotive industry nowadays is high-pressure RTM, which in combination with microwave heating can reduce production cycle down to 20 mins per part [1]. At the same time new materials are required to extend application range of the composites. One of the limitations of the polymer composites is quite low operation temperatures caused by the nature of matrices. Even typical heat-resistant matrices based on bis-maleimides [2,3], polyimides [4,5], benzoxazines [6,7], cyanate ether [8,9] can be use at temperatures up to 250-300 °C.

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Polymer matrices based on phthalonitriles are known for their resistance to high temperatures (T_g > 400 °C, $T_{5\%}$ > 500 °C) at the same time for poor processability due to which the only possible way to manufacture composites was to use prepregs obtained from the resin solution [10–15]. The development of low-melting monomers and oligomers was a long-term trend in a field of phthalonitrile resins [16–18]. In the case of oligomeric bis-phthalonitriles a good processability suitable for cost-effective resin injection methods of composite manufacturing was reached but at the same time a significant decrease in Young's modulus of the thermosets was observed [16,19]. With the development of siloxane- and phosphate-bridged bis-phthalonitriles [20,21] a manufacturing of carbon fiber reinforced plastics (CFRP) by cost-effective technologies such as VIMP and RTM (impregnation at 150 °C) was reported [22,23]. However, the reported composites demonstrated moderate mechanical properties which retained at 300 °C for 70-80%. Thus, an improvement of these materials was still demanded.

In the current report we introduce new bis-benzonitrile reactive diluents for phthalonitrile resins and describe resin formulations based on the phosphorus-containing monomers. Using VIMP at 120 °C and hot-pressing prepreg consolidation CFRP samples were manufactured and characterized in detail.

These results can widely extend the application range for composite materials in aerospace (for production of complex-shaped parts, e.g. jet engine blades or skin of ultrasonic vehicles) and other applications such as high-temperature composite tooling for thermoplastics processing, flame-retardant materials for interior parts of submarines, engine cowls, exhaust pipes etc.

2. EXPERIMENTATION

2.1 Materials and methods

All the monomers were obtained according to the procedures reported earlier. 1,3-bis (3,4-dicyanophenoxy)benzene (**5**) was synthesized according to the know procedure [24] with quantitative yield (98 %). Bis(3-(3,4-dicyanophenoxy)phenyl) phenyl phosphate was synthesized following the procedure described in [21]. Bis(4-cyanophenyl) phenyl phosphate was obtained as described in [25]. 3,3'-(1,3-phenylenbis(oxy))dianiline (APB) was purchased from SynAsia and used as received. Quartz flour Silverbond 30 and was purchased from Sibelco as used as it is. Carbon fabric 22502 from JSC INCMaT 2x2 twill wave from 3k HTA40 TohoTenax from Teijin fiber was used for CFRP preparation. Auxiliary materials for vacuum bagging were purchased from Airtech.

Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix, at a heating rate of 10°C/min and an Ar purge rate of 50 mL/min and was applied for Tg of the uncured resins determination and curing study. Thermal stability was evaluated by TGA on Netzsch TG 209 P3 Tarsus, at a heating rate of 10°C/min in range 40–980 °C and an argon or air purge rate of 50 mL/min. Heat deflection temperature (HDT) was measured by the three-point bending method according to ASTM-E2092-03 on Netzsch TMA 402 with 1.82 MPa loading. DMA was performed using TA Instruments DMA Q800 in three-point bending regime with 1 Hz frequency and amplitude 40 μm with heating rate of 5 K/min. Mechanical tests were carried out using Hounsfield H100KS, H5KS and Instron 5985 testing machine. The reported mechanical property values were based on an average of at least five tests. Determination of flexural mechanical properties was carried out using the three-point bending method according to the ASTM D790 at 1.28 mm/min crosshead rate

2.2 Curing

Curing of phthalonitrile resins for primary properties estimation was performed in a glass vials in a glovebox under atmosphere of Ar. The mixture was placed into a vial, melted and degassed at 120–180 °C by stirring under vacuum. Then the temperature was raised to 180 °C at the rate of 2 °C/min and kept for 6 hours. Then the temperature was raised up to 330 °C or 375 °C (10 K/h) and the samples were post-cured for 8h.

Samples for mechanicals tests were manufactured as follows: resin **PNT** (500 g) was placed into a 2 L glass reactor, then melted and degassed by mechanical stirring (200 rpm) under vacuum at 150 °C for 15 min. The melt was then poured into a metal mold, which was placed into an air circulated heated oven and cured for 6 hours at 180 °C. After that, the mold was disassembled, and the cured laminate was cut in two equal parts. One part was studied in cured state, the other was post-cured at up to 300-375 °C as described above.

2.3 Vacuum infusion processing

Stainless steel plate with dimensions 500×700×4 mm^3 coated with release agent (except for the edges) was used to produce CFRP by vacuum infusion process. Sealing tape was secured along the perimeter. Silicone rubber tubes for resin feed and evacuating channels were installed on the opposite edges of the plate. At the side of the feed channel 10 layers of 200 g/m^2 carbon fabric twill 2x2 (toho tenax HTA40) were placed and covered with peel ply and distribution medium. Further, vacuum film was attached to the sealing tape, the vacuum bag was placed in the oven, connected to the vacuum pump and heated to 120 °C. Upon reaching 10 mm. Hg inside the vacuum bag, degassed resin preheated to 120 °C was infused via feed channel. After 10–15 minutes the resin exited the vacuum bag into the vacuum channel, which indicated the end of impregnation. After the completion of the infusion process, the temperature was raised to 180 °C at the rate of 1 °C/min and held for 6 hours. Then the package was disassembled, and the cured sample was post-cured at 330-375 °C as described above.

2.4 PNT-P preparation

To prepare prepreg resin **PNT-P**, 25 kg of **PNT** was placed into a 100 l metal reactor, melted at 120 °C under vacuum (<1 mmHg) and stirring. Then 10 kg of quartz flour were mixed with the resin by adding a 2500 g parts of the flour followed by vigorous stirring under vacuum for 15 minutes. After mixing of each portion stirrer was stopped and vacuum was released to add the next portion of the flour. This procedure was repeated four times with final stirring for 30 mins under vacuum. After chilling down, 35 kg of light-green paste was obtained.

2.5 Prepreg fabrication and consolidation

To fabricate prepreg **PNT-P1** was placed on a carbon or glass fabric piece 30 × 30 cm and spread uniformly on its surface by hot ironing. Then 10 layers of carbon prepreg(8 layers of glass prepreg) were plied on a flat metal mold and sealed in a vacuum bag. Pre-form was placed into a heating press and plates temperature was increased up to 140 °C with heating rate 2 °C per minute. Than pressure of 8.75 bar was applied to a sample and temperature was raised up to 180 °C with heating rate 2 °C per minute. When the temperature reached 180 °C the applied pressure was increased to 20 bar and the sample was treated this way for 6 hours following with cooling down the apparatus down to 50 °C with rate 5 °C/min. After that the mold was disassembled and the sample post-cured in a free state according to procedure mentioned above with top temperature up to 330 °C for 8 hours.

3. RESULTS

In our recent works we reported synthesis of low-melting phosphate-bridged phthalonitrile monomers featured by increased thermo-oxidative stability [21]. Monomer **1** (Figure 1) was chosen among the phosphorus-containing as the most prospective for further applications due to the low T_g = 22 °C and optimal synthesis procedure. Monomer **1** (Figure 1) 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 possessed thermal properties at the same level as the common phthalonitrile monomer **2** (Figure 1) described earlier [24] and cured in the same conditions as **1**.

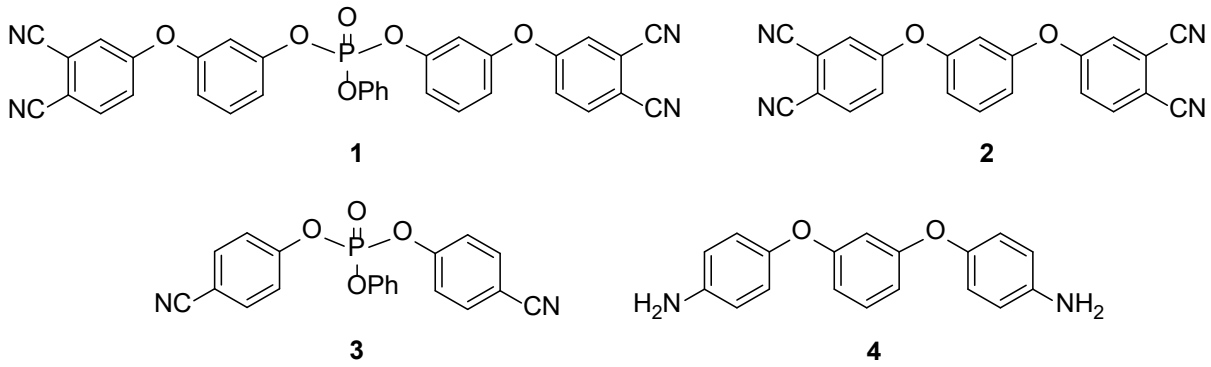


Figure 1. The monomers comprising PNT formulation

It is notable that the cured matrix obtained from **1** monomer demonstrated increased thermo-oxidative stability in comparison to cured monomer **2**. This effect could be explained by the presence of a phosphate group in the molecular structure of **1**. In the experimental conditions TGA the sample of cured **1** retained almost 30 % of the initial mass at 1000 °C in contrast to the sample of cured **2** which totally combusted at 800 °C (Figure 1).

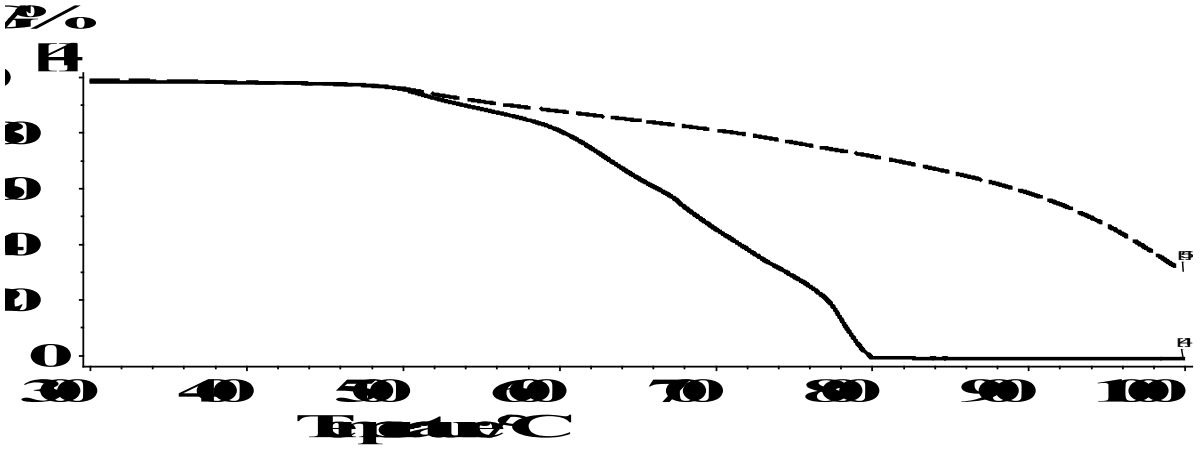


Figure 2. TGA curves of the cured monomers **1** (dashes) and **2** (solid) in air.

Using monomers **1** and **2** in combination with reactive diluent **3** (Figure 1) recently synthesized in our lab [25] and diamine **4** (APB) as curing agent, a formulation named **PNT** was developed.

Blended resin **PNT** demonstrated melt viscosity 1000 mPa·s 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 enough 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.

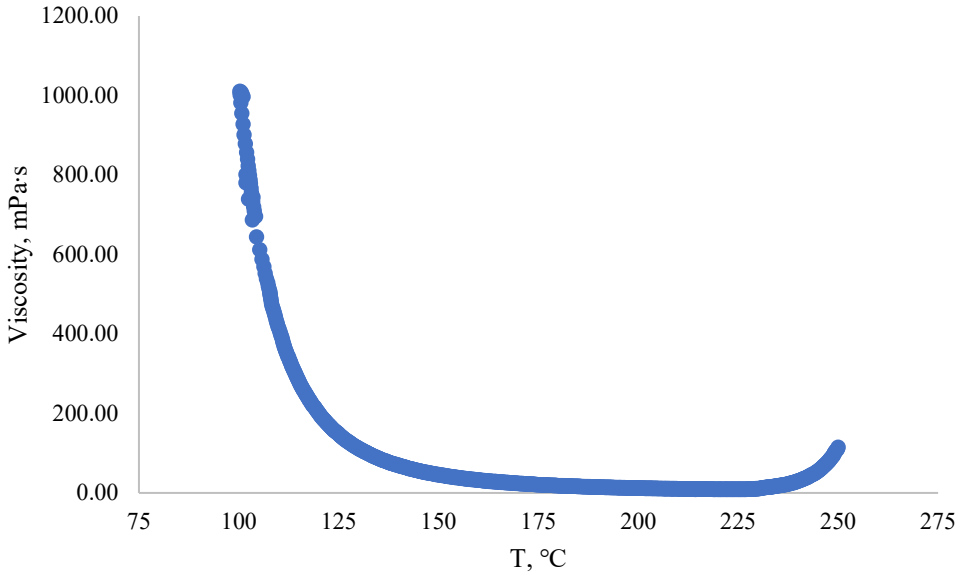


Figure 3. Viscosity profile of **PNT**

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 DMA) 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 plates 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 = 39-63 10^{-6} K^{-1}.

Table 1. Thermal properties of thermosets derived from **PNT**

Parameter	**Curing conditions**		
	6 h, 180 °C	**8 h, 330 °C**	**8 h, 375 °C**
T_g, °C	198	347	>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

3.1 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).

Table 2. Mechanical properties of the composites obtained by vacuum infusion

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	852	538
	E, GPa	ASTM D3039	67	60
Interlaminar shear strength	τ_{13}, MPa	ASTM D2344	53	44
In plane shear strength	τ_{12}, MPa	D3579	106	75
	E, GPa	D3579	6.0	5.7

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 τ_{13} = 38 MPa, demonstrating retention of mechanical properties 86% of the value at room temperature.

Table 3. Mechanical properties of the composites

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	50	95	43	75
350	46	88	41	69
400	–	–	38	68

3.2 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 63% and for CFRP more than 80% (the experiment was stopped due to the safety reasons) which are the highest values among the reported for any plastics.

Table 4. Flammability of CFRP with matrices of different types

Sample	**LOI, %**
PNT	63
CFRP (PNT based, VI)	>80

3.3 Prepreg fabrication and consolidation.

Resin **PNT** possessed T_g = 21°C and thus was suggested suitable for prepreg fabrication since at room temperature it was ductile and allowed to roll the prepreg. In order to reduce material cost and decrease the shrinkage effects and keep thermal performance, 40% of quartz flour was added to **PNT** to form resin assigned **PNT-P** as white green paste. The paste was spread on carbon fabric sheets by hot ironing and then 10-layer thick CFRP samples containing 42-45% of the matrix and 8-layer GFRP containing 37-40% of the matrix were obtained by hot-pressing processing. ILSS data depending on the curing conditions is given in Table 5. It is seen that reduction of the curing temperature results in increase of mechanical properties of the composites.

Table 5. ILSS values collected for prepreg originated CFRPs

T, °C	Vacuum infusion		CF, prepreg consolidation, vacuum	CF, prepreg consolidation, hot-pressing		GF, prepreg consolidation, hot-pressing
	8 h, 330 °C	8 h, 375 °C	8 h, 330 °C	8 h, 300 °C	8 h, 330 °C	8 h, 330 °C
25	53	44	41	50	41	50.7
300	50	43	35	44	41	38.0
350	–	41	31	–	33	27.7
400	–	38	21	–	26	–

4. CONCLUSIONS

Application of new class of reactive plasticizers allowed to obtain low-melting resin formulation **PNT** perfectly suitable for cost-effective injection methods of FRP manufacturing and for the first time for solvent-free prepreg obtaining. 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 up to 90 % at 450 °C and exceptional fire retardant properties due to the use of phosphorus-containing monomers. 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 for production of large-scaled and complex-shaped parts operating at elevated temperatures

First experiments of solvent-free prepreg fabrication and consolidation showed the possibility to apply this wide-spread technique for phthalonitrile resins. At the same time, more data should be collected for approval of the technology. Additional information on the topic will be presented in the conference.

ACKNOWLEDGMENTS

The work was supported by Government of the Russian Federation Ministry of Science and Higher Education. Contract No. 14.607.21.0204 (RFMEFI60718X0204)

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