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Flame-retardant carbon fiber reinforced phthalonitrile composite for high-temperature applications obtained by resin transfer molding

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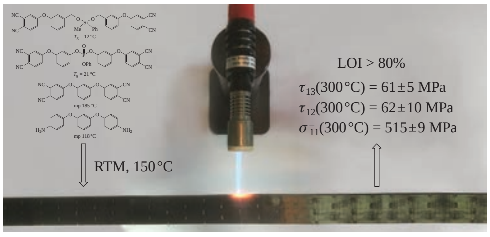
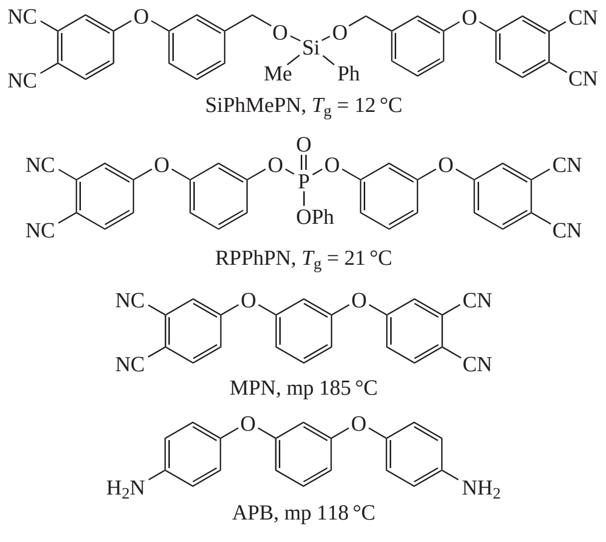
Carbon fiber reinforced phthalonitriles obtained by resin transfer molding have been reported for the first time. Special formulation based on silicon- and phosphorus-containing phthalonitrile monomers has been developed to yield a composite with retention of mechanical properties at 300 °C and remarkable flame-retardant properties (LOI > 80%).



Thermosets derived from phthalonitrile resins are known as the most heat resistant polymers. Therefore, they were considered as matrices for carbon fiber reinforced plastics (CFRP) since 1980s.[1–6] Nowadays, high-temperature composite materials are in demand for different high-tech applications, from aerospace to energetics. However, the applications of these resins were strictly limited due to a poor processability. Only a few works dedicated to phthalonitrile-based CFRP manufactured from prepregs are available.[6–8] Development of phthalonitrile oligomers resulted in resins with improved processability which is suitable for cost-effective injection methods of CFRP manufacturing,[9] but still no data dedicated to such composites were published. Development of low-melting phthalonitrile resins and cost-effective technologies of CFRP manufacturing could widely extend applications of composite materials in aerospace (for production of complex-shaped parts, *e.g.* jet engine blades) and other applications such as composite tooling for high-temperature CFRP production.


SiPhMePN, T_g = 12 °C

RPPhPN, T_g = 21 °C

MPN, mp 185 °C

APB, mp 118 °C

Figure 1 Chemicals for phthalonitrile resin formulation.

Previously we reported[10–13] that low-viscosity phthalonitrile formulations for resin transfer molding (RTM) or vacuum infusion molding process (VIMP) were prepared from the low-melting siloxane- and phosphate-bridged phthalonitrile monomers.

In this work, three monomers were applied for resin formulation (Figure 1). Siloxane-bridged SiPhMePN was chosen as monomer with the lowest viscosity,[14] while phosphorus-containing RPPhPN increased thermo oxidative stability of the resulting thermoset.[11] The main component MPN was chosen due to its availability and aromatic diamine APB was used as polymerization initiator.

The formulation PN-13 (25 wt% of SiPhMePN, 25 wt% of RPPhPN, 50 wt% of MPN) as well as 5 wt% APB were used for further experiments.[†] It was demonstrated during preliminary experiments that maximum content of MPN should not exceed 50% to reach low melt viscosity of the formulation. The processing parameters such as melt viscosity and pot-life were investigated.[‡] Viscosity–temperature curve is shown in Figure 2. Melt viscosity

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[†] All monomers were synthesized as described previously.[10,11,15] 1,3-Bis-(4-aminophenoxy)benzene (Sigma-Aldrich) was used as received. SiMePhPN (125 g), RPPhPN (125 g), and MPN (250 g) were placed into 2 dm^3 reactor equipped with anchor-stirrer. Reactor was heated to 150 °C until the mixture was melted and then degassed (5 Torr) under vigorous stirring for 30 min. After that 5 wt% of APB (25 g) was added to the mixture under vigorous stirring. The resin was degassed again and poured onto a metal surface, cooled in air and crushed to 1–5 cm glassy pieces.

[‡] Melt viscosity was measured using Brookfield C2000+ Viscometer with cone 10 at 40 rpm. Viscosity–temperature curve was recorded in the range of 100–235 °C with heating rate of 2 K min^{-1}. Pot-life was determined in isothermal experiment at 150 °C and assigned to the time of a drastic viscosity growth.

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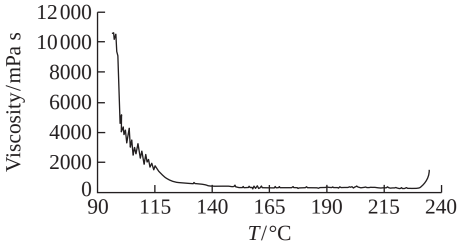

Figure 2 Viscosity–temperature curve for formulation PN-13.

Table 1 Thermal properties of cured phthalonitrile monomers and resin PN-13.

Monomer	HDT/°C	$T^{\mathrm{Ar}}_{5\%}$/°C	$Y^{\mathrm{Ar}}_{\mathrm{c}}$ (%)	$T^{\mathrm{Air}}_{5\%}$/°C	$Y^{\mathrm{Air}}_{\mathrm{c}}$ (%)	Ref.
SiMePhPN	424	549	80	524	12	10
RPPhPN	455	524	80	524	29	11
MPN	441	523	75	504	0	15
PN-13	418	517	75	508	7	This work

was lower than 150 mPa s at temperatures over 140 °C and fast polymerization started at 230 °C. It was determined that viscosity remained at the same level for more than 12 h at 150 °C, in so far as PN-13 was suitable for RTM processing.

Samples of the resin were cured[§] to investigate their thermal properties (Table 1). High thermal properties of blended formulation PN-13 were demonstrated to retain owing to phthalonitriles in contrast to low-viscous oligomers resulting in the polymer with decreased thermal properties.[9] Heat deflection temperature (HDT) was 418 °C due to the presence of silicon-containing monomer SiMePhPN. Decomposition parameters [temperature of 5% weight loss in Ar and in air ($T^{\mathrm{Ar}}_{5\%}$, and $T^{\mathrm{Air}}_{5\%}$, respectively), and char/ash yield ($Y^{\mathrm{Ar}}_{\mathrm{c}}/Y^{\mathrm{Air}}_{\mathrm{c}}$)] were defined by MPN, although ash yield was still higher than theoretical SiO_2 content in the combustion residue due to the presence of flame-retardant monomer RPPhPN.

Flexural properties of the cured resin PN-13 were evaluated (Table 2).[¶] According to the data presented below, flexural strength of the resin PN-13 is on the same level as compared to the other reported phthalonitrile matrices based on silicon- and phosphorus-containing monomers. The value of the flexural modulus is high despite of the presence of SiPhMePN. Apparently, resins with 50% MPN content possessed the highest values of flexural modulus.

Thus, combination of processing properties of uncured resin and thermal properties of the thermoset has confirmed that PN-13 is prospective for CFRP manufacturing.

Table 2 Flexural properties of phthalonitrile resins.

Matrix	Flexural strength/MPa	Flexural modulus/GPa	Ref.
PN-13	83±13	5.6±0.1	This work
SiPhMePN	69	2.6	14
SiPhMePN/MPN (30:70)	76	4.0	14
RPPhPN/MPN (30:70)	75	4.5	11
RPPhPN/MPN (50:50)	70	5.6	11

Table 3 Mechanical properties of the CFRP based on PN-13 obtained in this work.

T/°C	τ_{13}/MPa	τ_{12}/MPa	σ^{-}_{11}/MPa
25	72±7	63±6	767±30
300	61±5	62±10	515±9
Δ (%)	–15.3	–1.5	–22.4

The samples of CFRP were obtained using the PN-13 resin by vacuum-assisted RTM technique.[††] Resin injection and impregnation were performed at 150 °C to the metal mold filled with carbon fiber UD tape placed in oven.

Composite plate with 25% resin content was obtained after post-curing and used to study mechanical properties. The loss of mechanical properties at 300 °C was 15–30% depending on the test type (Table 3). The value of interlaminar shear strength (τ_{13}) confirmed high integrity of the material and inspite of 15% decrease at 300 °C remained at sufficiently high level indicating high thermal stability of the composite.[‡‡] The decrease in compressive strength (σ^{-}_{11}) due to heating was 20%, however the value at 300 °C still allows one to consider this composite as high-temperature constructive material.

To minimize damage in case of fire, indoor applications such as interior aircraft panels or composite tooling require flame-retardant materials. Limiting oxygen index (LOI)[§§] of phthalonitrile composite based on PN-13 was found to be higher than 80%. Further increase in oxygen concentration in the experiment was stopped for safety reasons. Anyway, this value is the highest for reported CFRP with different polymeric matrices (Table 4).

Thus, for the first time CFRP based on phthalonitrile resin has been obtained by RTM method. Mechanical properties of the material at 300 °C allow us to consider it as high-temperature

Table 4 Flammability of CFRP with matrices of different types.

CFRP matrix type	LOI (%)	Ref.
Epoxy	24–31	16, 17
Epoxy + flame retardant agent	30–50	16, 17
Benzoxazine	26	18
Benzoxazine + pyromellitic dianhydride	<49.5	18
Novolac/DAEBA	>55	19
PN-13	>80	This work

[§] PN resin (1 g) was placed into glass vial, melted and degassed at 130–150 °C (1 Torr). Then the vial was filled with Ar and the sample was heated (2 K min^{-1}) up to 250 °C (6 h), 315 °C (6 h), and 375 °C (8 h).

[¶] Determination of flexural mechanical properties was carried out using three-point bending method according to ASTM D790 at 1.28 mm min^{-1} crosshead rate using Hounsfield H100KS, H5KS and Instron 5985 testing machines. The reported mechanical property values were based on an average of seven tests.

[††] Unidirectional carbon tape with (IMS65, 24K, 280 g m^{-2}) was cut into rectangular pieces (20 × 30 cm) and put in the stainless steel mold.[14] Solid resin (300 g) was placed into a feeding tank connected to the mold and a compressor on the opposite side. The mold outlet was connected to the vacuum pump. The system was placed in an oven, heated to 120 °C and then a vacuum pump was applied to get pressure of 0.75 Torr. The mold was heated to 150 °C and the pressure of 1 bar was settled in the feeding tank. The pressure was increased to 3 bar in 40 min and when the resin appeared in an outlet tube the mold was vented. After treatment at 220 °C for 12 h the mold was disassembled and CFRP sample was post-cured according to the temperature program described above for small samples.

[‡‡] The mechanical properties were investigated using Instron 5985 and Hounsfield H100KS testing machines with environmental chamber at 300 °C. All specimens were prepared from cured laminates *via* precision cutting by CNC milling machine. Compression strength was measured according to ASTM D6641. The interlaminar shear strength was measured by the short-beam method according to ASTM D2344. In-plane shear strength was tested according to ASTM D5379. At least 7 specimens were examined under the test conditions. During the test at elevated temperature, the specimen inserted in fixture was heated to 300 °C and was kept for 30 min at this temperature prior to start. It provided for uniform heating through the laminate thickness. The temperature on the sample surface during the test was controlled by thermocouple.

[§§] LOI was determined according to GOST 12.1.044-89 procedure.

composite for wide range of applications. Extremely high LOI makes its indoor applications such as interior aircraft panel very attractive.

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