

## Carbon fabric reinforced propargyl ether/phthalonitrile composites produced by vacuum infusion

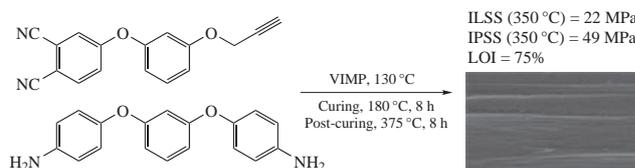
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Heat-resistant polymer composites were obtained from 4-[3-(prop-2-yn-1-yloxy)phenoxy]benzene-1,2-dicarbonitrile and carbon fabric by a vacuum infusion molding process. The composite materials demonstrated the retention of mechanical properties down to 80% at 350 °C and low inflammability (limiting oxygen index, 75%).



Carbon fiber reinforced plastics (CFRPs) are common materials in aerospace, automobile production, sports industry, etc. The application of polymer composites at elevated temperatures is limited and traditional materials are predominant in the production of jet engine parts and tooling for CFRP formation. Operation temperatures for polymer composites are defined by polymer matrices and the development of such resins as bismaleimides<sup>1–3</sup> and polyimides<sup>4–6</sup> allowed one to increase the operation temperatures to 250–300 °C. Phthalonitriles are the most heat resistant polymers, however due to poor processing properties only composites developed from prepregs (produced by a solution technique) were reported.<sup>7–9</sup> The development of phthalonitrile resins suitable for out-of-autoclave CFRP production techniques<sup>10–17</sup> made it possible to obtain new heat-resistant and flame retardant composites by vacuum infusion molding<sup>18</sup> and resin transfer molding.<sup>19</sup> As an alternative approach to the design of new resins for out-of-autoclave processing, hybrid monomers containing two thermosetting groups (phenolic propargyl ether and phthalonitrile) were reported.<sup>20</sup> Previously, it was shown that aromatic propargyl ether groups initiate the polymerization of phthalonitriles resulting in heat-resistant thermoset formation.<sup>21,22</sup>

In this work, we prepared composites from the recently developed monomer 4-[3-(prop-2-yn-1-yloxy)phenoxy]benzene-1,2-dicarbonitrile (PPN) (Figure 1)<sup>20</sup> and carbon fabric by a vacuum infusion molding process (VIMP). The composites demonstrated moderate mechanical properties along with excellent temperature resistance; thus, they can be suitable for composite

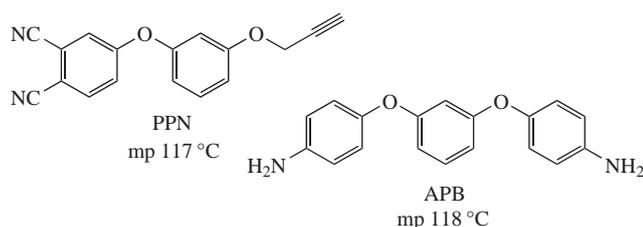


Figure 1 Thermosetting monomer PPN and curing initiator APB.

Table 1 Mechanical properties of the PPN resin cured under different conditions.

| Matrix                   | HDT/<br>°C | Flexural<br>strength/<br>MPa | Flexural<br>modulus/<br>GPa | $G_{1C}/J\ m^{-2}$ | $K_{1C}/MPa\ m^{1/2}$ |
|--------------------------|------------|------------------------------|-----------------------------|--------------------|-----------------------|
| PPN                      | 432        | 73±8.5                       | 4.5±0.24                    | 52±2               | 0.31±0.03             |
| PPN + 4% APB             | 418        | 60±7.8                       | 4.9±0.65                    | 106±6              | 0.43±0.05             |
| PPN + 10% APB<br>(PPN10) | 412        | 85±7.3                       | 5.1±0.26                    | 97±3               | 0.52±0.05             |

tooling manufacturing, jet engine blades production or skin for hypersonic aircrafts.

The mechanical properties of PPN blended with APB were estimated (Table 1).<sup>†</sup> For this purpose, the PPN monomer was melted in a glass reactor, mixed with a proper amount of APB, degassed (1 Torr, 130 °C, 30 min) and casted to a metal mold. Curing was performed by heating at 180 °C for 12 h; then, the temperature was raised (10 K h<sup>-1</sup>) to 375 °C with a final exposure for 8 h.

The mechanical properties and fracture toughness parameters of the polymers increased with the APB content. An increase in the APB content facilitated phthalonitrile polymerization resulting in the formation of a cross-linked stiff network. The best properties were found for a formulation containing 10% APB, which is referred to as PPN10.

According to the dynamic mechanical analysis of PPN10, there is no clear transition on the curve but around 400 °C the storage modulus drastically decreases (see Online Supplementary Materials). Anyway, mechanical properties of the thermoset allow us to consider the formulation as a matrix for CFRP.

The processing properties of PPN10 were estimated by viscosity measurements. Melt viscosity of PPN at 130 °C was 45 mPa s and reached a plateau (~35 mPa s) at 140 °C. At 180 °C gelation time of the resin was ~7 h, which together with low viscosity at

<sup>†</sup> Experimental conditions for mechanical tests are given in Online Supplementary Materials.

130 °C provides proper processibility for cost-effective injection.<sup>†</sup> Impregnation was performed in a programmable oven equipped with a vacuum pump at 130 °C for about 15 min. After the resin showed up in the outlet tube outside the oven, it was sealed and heated at 180 °C for 8 h. The sample was disassembled and post-cured at 375 °C to afford high-temperature CFRP with a matrix content of 28–30%.

First, we manufactured samples with standard epoxy-sized carbon fabric by vacuum infusion. Interlaminar shear strength values indicated an average level of adhesion between fabric and resin. However, it was suggested that epoxy sizing, which coated fibers of the fabric, could decompose during post-curing and affect mechanical properties. To check this suggestion, carbon fabric without a sizing agent was examined. Surprisingly, this sample demonstrated mechanical properties similar to those of the sample with sizing. Probably, during the impregnation process, the sizing was dissolved in the resin and washed out from the fabric by the resin flow.

To provide higher mechanical parameters, the CFRP samples impregnated by vacuum infusion molding were cured in a heating press under 203 kPa (2 atm). The pressed samples revealed the highest mechanical characteristics among the considered CFRP samples.

The mechanical properties of VIMP manufactured phthalonitrile/carbon textile composites were reported.<sup>18</sup> Both of the CFRPs were composed of phthalonitrile matrices formulated from a low-melting phosphorus-containing monomer and 1,3-bis-(3,4-dicyanophenoxy)benzene in combination with APB. The PN-3 matrix also contained PPN resin as a reactive diluting additive. The composites possessed mechanical properties similar to those of reported materials although somewhat lower than those of PN-3 based CFRP (Table 2).

The thermal behavior of the composites was estimated by shear strength tests at elevated temperatures (Table 3). The materials retain down to 82% of mechanical properties at 300 °C and 70–75% of the interlaminar shear strength at 400 °C. These data are in accordance with DMA curve where harsh decrease in storage modulus was observed around 350 °C (Figure S1, Online Supplementary Materials). In the PPN10 based composite obtained by VIMP with pressing, the retention of  $\tau_{13}$  and  $\tau_{12}$  at 300 °C was 93 and 91%, respectively. For CFRPs based on PN-2 and PN-3, these values were 97%/98% and 95%/93%, respectively, for

**Table 2** Mechanical properties of the CFRP samples.

| Sample                    | Tensile strength     |         | Compressive strength |        | Inter-laminar shear strength $\tau_{13}$ /MPa | In plane shear strength $\tau_{12}$ /MPa |
|---------------------------|----------------------|---------|----------------------|--------|---|--|
|                           | $\sigma_{11}^+$ /MPa | E/GPa   | $\sigma_{11}^-$ /MPa | E/GPa  |   |  |
| Epoxy sizing              | 548±14               | 67±1.9  | 325±22               | 63±3.6 | 32±2.8  | 57±3.6                                   |
| No sizing                 | 571±19               | 67±0.12 | 277±19               | 61±2.4 | 26±2.9  | 54±1.9                                   |
| Epoxy sizing, pressing    | 556±15               | 65±0.8  | 401±17               | 60±2.6 | 28±2.3  | 65±1.7                                   |
| PN-2 matrix <sup>18</sup> | 487±17               | –       | 341±36               | –      | 31±2  | 66±1.7                                   |
| PN-3 matrix <sup>18</sup> | 669±16               | –       | 429±36               | –      | 37±3  | 78±2.6                                   |

**Table 3** Mechanical properties of the composites at elevated temperatures.

| T/°C | Epoxy sizing     |                  | No sizing        |                  | Epoxy sizing, pressing |                  |
|------|------------------|------------------|------------------|------------------|------------------------|------------------|
|      | $\tau_{13}$ /MPa | $\tau_{12}$ /MPa | $\tau_{13}$ /MPa | $\tau_{12}$ /MPa | $\tau_{13}$ /MPa       | $\tau_{12}$ /MPa |
| 300  | 25±3.1           | 54±2.5           | 23±2.4           | 49±2.0           | 26±2.3                 | 59±1.1           |
| 350  | 25±2.7           | 47±2.7           | 22±3.2           | 49±1.7           | 25±2.1                 | 53±2.1           |
| 400  | 23±1.8           | 37±0.95          | 18±1.7           | 41±3.0           | 22±1.2                 | 42±1.3           |

**Table 4** Flammability of phthalonitrile matrices, based on them carbon fabric composites as well as CFRP with different matrices.

| Sample             | LOI (%) | Reference |
|--------------------|---------|-----------|
| PPN                | 41      | This work |
| PN-3M              | 61.5    | 23        |
| CFRP (PPN based)   | 75      | This work |
| CFRP (PN-3M based) | 79      | 23        |
| CFRP (PN-13 based) | >80     | 19        |
| CFRP (Epoxy)       | 25–50   | 24, 25    |
| CFRP (Benzoxazine) | 26–49.5 | 26        |
| CFRP (Phenolic)    | >55     | 27        |

$\tau_{13}/\tau_{12}$ . Thus, taking in account the roughness of measurements, we can conclude that the same level of strength retention is observed for all of the considered materials.

In the case of materials for high-temperature indoor applications, e.g., composite tooling, additional requirements such as fire resistance should be fulfilled. Samples of the cured matrix and CFRP were tested for limiting oxygen index (LOI) according to the Russian GOST (State Standard) 21793-76. Both of the materials showed LOI values lower than those for phosphorus-containing phthalonitrile matrices but still higher than those for the known polymer materials (Table 4).

The CFRP samples were obtained based on the resin PPN10 and carbon fabric by vacuum infusion molding at 130 °C, which is the lowest temperature reported for phthalonitriles. The developed materials demonstrated high flame resistant properties: the LOI of CFRP samples was 75%, which makes them suitable for indoor applications. Thus, due to the easy processing and fire resistance, such materials are prospective for aerospace or other fields that require materials with extended thermal performance.

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#### Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.01.014.

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