Dual-curing propargyl/phthalonitrile monomers for composites by vacuum infusion process

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Abstract. Four different bifunctional monomers were synthesized: two monomers containing N-propargylamine and phthalonitrile groups and two monomers containing O-propargyl ester and phthalonitrile groups. It was shown that only the latter one can be used to obtain composite materials by vacuum infusion (viscosity 40 mPa*s at 120 °C). The N-propargylamine containing monomers demonstrated high viscosity of the melts and degradation with allene evolution while curing. Carbon fiber reinforced plastics (CFRP) were successfully obtained from 4-[3-(prop-2-yn-1-yloxy)phenoxy]benzene-1,2-dicarbonitrile by a vacuum infusion molding process. Mechanical testing of the composites samples was performed. Influence of end-curing temperature on mechanical properties and morphology of composites was investigated. The curing temperature of 375 °C critically affects the properties of the composite due to the high shrinkage. Composites cured at 375 °C lost 18% of mechanical properties at 300 °C but cured at 330 only 10%. LOI for composites with a matrix of propargyl/phthalonitrile dual-curing polymers was equal to 75, which is higher than most materials obtained from thermosets.

Keywords: Carbon composites, vacuum infusion, phthalonitriles, propargyl resins, thermosetting copolymers.

Introduction

The use of composite materials in applications ranging from aerospace structures to automotive and marine applications instead of conventional materials is of great interest. Advanced composites show a wide range of desirable properties such as high stiffness and strength, dimensional stability, temperature resistance, and easy processing. One of the most efficient techniques in manufacturing of such composites is injection methods such as vacuum infusion (VIMP) and resin transfer molding (RTM). The main reasons why these methods have recently become so attractive in the fabrication technology are low cost of tooling and scalability to very large structures. VIMP and RTM also allows to minimize the void contents inside the composites what results in less defects content leading to the increase of mechanical properties of composites comparing to other molding techniques [1].

The development of bifunctional polymers with two types of thermosetting functional groups allows to vary the properties of polymer such as melting point, viscosity, curing conditions and customize them for a particular task [2]. It is known that phthalonitrile polymers have the best value of heat resistance among thermosetting polymers of high-temperature use. However, phthalonitrile monomers are often characterized by high melting and polymerization temperatures, which complicates the formation of composites. In addition, a high degree of crosslinking decreases the mechanical properties of phthalonitrile polymers. The introduction of additional functional groups in the polymer, such as propargyl, allows to eliminate the above-mentioned disadvantages of...
phthalonitrile polymers. Propargyl groups are of great interest as functional groups for modifying the polymers, primarily due to the final properties of the polymer obtained, its high mechanical characteristics and thermal stability. There are few reports about the possibility of copolymerization of propargyl and phthalonitrile groups [3,4]. It is assumed that intermediates formed during the Claisen rearrangement can react with phthalonitrile fragments through OH-groups. This copolymerization allows to decrease greatly the curing temperature of phthalonitrile without loss of properties.

**Monomer Synthesis**

All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. All the solvents were purchased from Alfa Aesar and purified according to the standard procedures.

![Figure 1. Scheme of synthesis propargyl/phthalonitrile bifunctional monomers PPN-1, PPN-2, PPN-3, PPN-4.](image)

Monomers PPN-1 and PPN-2 was synthesized according to a two-step scheme (Figure 1). In the first step, precursor 1 or 2 reported earlier [5] was obtained by the reaction between hydroquinone or resorcinol and 4- nitrophthalonitrile. The second step was Williamson reaction between 1 or 2 and propargyl chloride in DMAc in the presence of K2CO3. The product was obtained with a total yield of 77% to 4-nitrophthalonitrile and characterized with 1H NMR spectroscopy and DSC.

Monomers PPN-3 and PPN-4 were synthesized in similar ways but for the alkylation reaction acetonitrile was used instead of DMAc as solvent according to the method described in Ref. [6].

**Analytical Methods.**

NMR spectra were run on Bruker Avance 600 at 600 MHz for 1H and 125 MHz for 13C with DMSO-d6 as solvent. Melt viscosity was measured with MCR 302 Rheometer with cone 10 at 200 t/min. Composite density was measured with Vibra ht-220-CE according to hydrostatic weighing method in pure octane. STA data for samples mass loss was measured with Netzsch STA 449 at a heating rate of 10°C/min in range 40–980°C and an Ar or air purge rate of 50 mL/min. SEM microphotographs were obtained using Vega 3 (Tescan) microscope with a lanthanum hexaboride cathode and secondary electron detector at operating voltage of 20kV. Differential scanning calorimetry (DSC) was performed on Netzsch DSC 449 at a heating rate of 10°C/min and an Ar purge rate of 50 mL/ min.

**Mechanical Testing**

Interlaminar and in plane shear strengths were measured with Tinius Olsen 50ST according to GOST 32659-2014. Compressive, tensile strengths and elasticity modulus were measured with Instron 5985 according to GOST 9550-81.
Vacuum infusion molding process (VIMP).
Carbon fabric 22502 from JSC INCMaT 2 × 2 twill wave from 3k HTA40 TohoTenax from Teijin fiber was used for CFRP preparation. Auxiliary materials for vacuum infusion were purchased from Airtech.
Vacuum infusion process was used to manufacture CFRP samples. Synthesised resin PPN-2 were used. The full process of infusion was described earlier [7]. Vacuum infusion process was performed at 120°C. Curing process was conducted at 180°C, 12h and post-curing was conducted at 375 °C (C-1) or 330 °C (C-2).

Results and Discussion
It’s necessary that the resin has viscosity less than 800 mPa·s in order to be applied in vacuum infusion process. All four investigated resins satisfy this requirement at 130 °C beyond its melting point (Table 1). However the viscosity of PPN-3 resin is the highest of these four monomers. It was found that resins PPN-3 and PPN-4 are in accordance with Carnelley’s rule which runs as follows: high molecular symmetry is associated with high melting point [8]. However for PPN-1 and PPN-2 this rule does not work. Perhaps this occurs due to the formation of intermolecular hydrogen bonds, as mentioned in works dedicated to phthalonitriles, in which uncharacteristic dependences of the melting point on the structure of molecules are also observed [9,10].

Table 1. Rheological and curing properties of investigated monomers.

| Monomers | T_m, °C | Viscosity at 130 °C, mPa·s | Curing parameters |
|----------|---------|--------------------------|------------------|
|          |         |                          | T_onset, °C | T_max, °C | ΔH, J/g |
| PPN-1    | 98      | 39                       | 244          | 282       | 877     |
|          |         |                          |              | 303       |
| PPN-2    | 116     | 47                       | 242          | 283       | 800     |
|          |         |                          |              | 301       |
| PPN-3    | 133     | 567                      | 243          | 288       | 1001    |
|          |         |                          |              | 298       |
| PPN-4    | 88      | 56                       | 245          | 287       | 1094    |
|          |         |                          |              | 308       |
The melting points were found by endothermal pick from DSC-curve (Figure 2).

![DSC-curves of investigated monomers.](image)

Figure 2. DSC-curves of investigated monomers.

For all monomers, a first exothermal broad peak at 285 °C is observed at DSC-curves, which relates to the copolymerization reaction described above [11]. The second one at 305 °C corresponds to the polymerization of phthalonitrile fragments. It was found that aminopropargyl resins PPN-3 and PPN-4 can’t be cured without using any catalysts, because the degradation with allene emission occurs before reaching the temperature of curing (Figure 3). It’s observed that the addition of trimerization and Claisen rearrangement of propargyl groups catalysts [12,13] decreases the allene emission but leads to rapid polymerization after the melting point (Figure 4). Therefore catalyst introduction is not suitable for obtaining composite by vacuum infusion. This process requires using resins which features low viscosity under melting point for the time of infusion. Monomer PPN-4 showed similar behavior as PPN-3.

![TGA-curves of PPN-3 resin.](image)

Figure 3. TGA-curves of PPN-3 resin.
Figure 4. DSC-curves of aminopropargyl containing monomer PPN-3.

PPN-1 and PPN-2 resins were cured by following temperature program 180 °C – 8 h; 200 °C – 3 h; 220 °C – 3 h; 300 °C – 3 h; 330 °C – 3 h; 375 °C – 3 h. PPN-3 and PPN-4 resins were cured by the same program at another end-temperature 350 °C in the presence of ZnCl₂, while the void formation during curing was practically absent. Thermal properties of all obtained resins are presented in table 2.

Table 2. Thermal properties of the thermal cured monomers (PPN-3 and PPN-4 cured in the presence of ZnCl₂)

| monomers  | T₅%, °C | Yₓ, 900°C, % | Tₓ, °C |
|-----------|---------|--------------|--------|
| PPN-1     | 465     | 70           | 380    |
| PPN-2     | 451     | 72           | 432    |
| PPN-3     | 442     | 68,1         | 376    |
| PPN-4     | 421     | 63,7         | 352    |

Thus, the curing without decomposition of propargylated phthalonitrile amines PPN-3, PPN-4 is possible only in the presence of catalysts. Their thermal properties are superior to common propargyl resins [14], but they are inferior to polymers obtained from PPN-1 and PPN-2 propargyl monomers.

Based on thermal properties, viscosity and cure data resin PPN-2 was chosen for composites manufacturing by VIMP. The CFRP were obtained from a mixture of PPN-2 and 10 % mass. 1,3-bis(4-aminophenoxy) benzene (APB). In our previous work the best properties were found for such formulation containing 10% APB [15]. Composites obtained by vacuum infusion process were post-cured at two different temperatures 375 °C (C-1), (typical temperature for phthalonitrile curing) and 330 °C (C-2). The mechanical properties of post-cured composites were tested; the results are
presented in table 3. LOI for composites C-1 and C-2 was equal to 75, which is higher than most materials obtained from thermosets.

**Table 3. Mechanical properties of composite post-cured at 375 °C and 330 °C.**

| Mechanical tests | C-1 (375 °C post-cured) | C-2 (330 °C post-cured) |
|------------------|-------------------------|-------------------------|
| $\sigma_{11}$, MPa/ E, GPa | 548±14/67±1,9 | 742±15/62±0,9 |
| $\sigma_{11}'$, MPa/ E, GPa | 325±22/63±3,6 | 485±39/59±8,4 |
| $\tau_{13}$, MPa, 25 °C | 32±2,8 | 32±2,2 |
| $\tau_{12}$, MPa, 25 °C | 57±3,6 | 72±1,5 |
| $\tau_{13}$, MPa, 300 °C | 25±3,1 | 30±1,7 |
| $\tau_{12}$, MPa, 300 °C | 47±2,7 | 59±3,0 |

The tensile strength of C-2 obtained at a maximum curing temperature 330 °C is about 50 % higher than C-1, obtained at a maximum curing temperature 375 °C. At the same time, for sample C-2, no microcracking are observed in the SEM images (Figure 5), this can be related to the decrease of shrinkage for composite cured at lower temperature [16]. Indeed the volume shrinkage of the PPN-2 resin during curing at 330 °C was found 0.63%, while curing at 375 °C - 5.6%.

![Figure 5. SEM microphotographs of C-1 and C-2 composites, made by different curing temperature.](image-url)
Conclusions
CFRP were obtained from propargyl/phthalonitrile bifunctional monomer by vacuum infusion and the influence of post-cured temperature on mechanical properties and thermostability was investigated. It was found that the optimal post-cured temperature is 330 °C, this temperature provides no shrinkage while curing. The obtained composite retains good mechanical properties at 300 °C. It was established that aminopropargyl resins can’t be cured without using any catalysts, curing resins were obtained using ZnCl2. Their thermal properities were investigated.

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