Carbon Fabric Reinforced Addition-Cure Phenolic Resins Based on Propargyl and Allyl Ether Functional Novolac Produced by Vacuum Infusion

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Article info	Abstract
	Composites consisting of propargyl- and allyl/propargyl- modified novolac resins and carbon fabric were obtained by the vacuum infusion molding process. It was established that the presence of potassium cations remaining after the synthesis increase the resin melt viscosity, and acid washing is needed to obtain resins suitable for cost-effective injection techniques of composite fabrication. The mechanical properties of all composites such as compressive strength, tensile strength, in plane shear strength, and interlaminar shear strength were determined at 25, 200 and 230 °C. The carbon fiber reinforced plastics (CFRPs) retained their mechanical properties at temperatures up to 200 °C. It was shown that the use of the obtained allyl-containing polymer matrices improved mechanical properties and increased the thermal stability of the CFRPs in comparison with the propargylated novolac matrices. The composite material with novolac matrices modified by 18% propargyl and 23% allyl groups retains only up to 70% of the initial inter laminar shear strength values at 230 °C which corresponds to the data of the dynamic mechanical analysis of neat cured resins.

1. Introduction

Carbon fiber reinforced plastics (CFRPs) are materials widely used in aircraft and marine production, sports industry, etc. Vacuum infusion molding process (VIMP) has been considered as an attractive method to produce CFRP composites with low cost and good performance [1]. However, VIMP process requires low viscosity of the molding resin. At the same time the operating temperature of the molding process for polymer composites depends on the nature of the polymer matrix [2–4]. Epoxy resins most commonly used for VIMP, are characterized by relatively low thermal stability and high water absorption.

The phenolic resins modified by additional curable groups are of great interest due to improved heat resistance and better processability in deriving void-free composites [5]. Propargyl ether-functional phenolic resins were designed to substitute for the epoxy resins in cases when a hydrophobic material is needed [6]. Although propargyl resins were considered suitable to produce CFRPs by the VIMP process since the viscosities of the reported resins were suitable for injection processing [7, 8], no reports were dedicated to such materials. The main disadvantage of propargyl resins is the high curing exotherm (about 900 J/g), which requires a low heating rate in molding processes [9]. In this case, the use of a proper curing temperature program and careful process parameters control are indispensable. As a rule, it requires a lot of time and effort. [10]. There are many reports on the introduction of additional functional groups into propargyl resins aimed at reducing the curing exotherm or improving thermosets properties such as: phthalonitrile groups [11–13], azo-groups [14], benzoxazines [15, 16], and epoxy groups [17]. In our previous work, it was shown that the introduction of additional allyl groups into the propargyl phenolic resin structure reduces the heat release during curing without degrading the properties of the resulting

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polymer matrix [18]. Therefore, we hypothesized that CFRPs with a matrix of phenol-formaldehyde resins modified with both allyl and propargyl groups would be characterized by high mechanical properties and good processability.

2. Experimental

2.1. Materials

Novolac phenolic resin was obtained from Metadynea LLC (M_w = 3860 g/mol, Moscow, Russia) and used as received. Propargyl chloride, allyl chloride, potassium carbonate (K_2CO_3), dimethylacetamide (DMAc), isopropanol, and methylene chloride (all are of 99.9% grade) were obtained from Aldrich and used without additional purification. Carbon fabric 22502 from JSC INC-MaT (Moscow, Russia) 2×2 twill weave from 3k HTA40 TohoTenax from Teijin fiber (σ = 4 GPa, E = 240 GPa) was used for preparation of all composites. Consumables for vacuum infusion were purchased from Airtech (California, USA).

2.2. Methods

TA Instruments DMA Q800 (TA Instruments, USA) was used for dynamic mechanical analysis (DMA) performing in a 3-point bending mode with amplitude 40 μm with a heating rate of 5 K/min and 1 Hz frequency. The melt viscosity was measured with Brookfield C2000p Viscometer with cone 7 at 200 rpm. ^{1}H NMR spectra were recorded at 600 MHz with Bruker Avance 600 NMR instrument (Bruker, Germany) with DMSO-d6 as a solvent. The measurements of weight were performed using Sartorius Kern 770 (The Sartorius Group, Germany) analytical balance with a resolution of 0.1 mg.

Compressive, tensile and shear tests of CFRP were performed on Instron 5985 (Instron, USA) and Hounsfield H100KS systems (Hounsfield Test Equipment LTD, UK), with an environmental chamber for testing at extreme temperatures 200–400 °C. All testing samples were prepared from the composites obtained by milling on a CNC machine (Router 1390, Router, Russia) or cutting by a circular saw with a diamond wheel. The interlaminar shear strength (τ_{13}) was measured according to ASTM D2344 by the short beam shear test method. Tension tests (σ_{11} +) of samples (250×25 mm) were carried out according to ASTM D 3039 at a speed of 2 mm/min. Compression strength (σ_{11} -) was measured according to ASTM

D 6641, samples (140×12 mm) were compressed at a constant rate of 1.2 mm/min. V-notched rectangular samples (76×19 mm) were analysed to determine in-plane shear strength (τ_{12}) according to the ASTM D 5379 at a constant speed of 1 mm/min. At least seven samples were prepared for each specific testing condition. The sample was inserted in the clamp and heated to the desired temperature for testing at elevated temperatures than for uniform heating through the composite thickness. All samples were kept at an appropriate temperature for 30 min before starting the test. A thermocouple was used for controlling the temperature during testing.

2.3. Resin synthesis

Novolac resins modified by allyl and propargyl groups were synthesized as described in our previous work [18] (Fig. 1). The alkylation was carried out with 1.3 mole excess of propargyl and allyl chloride. Conversions of propargyl and allyl chlorides were 80% or more, which was estimated by analysis of ^{1}H NMR spectra.

PN-50: ^{1}H-NMR (600 MHz, δ, ppm, DMSO-d6): 9.31 (br.s., 1.01 H, -OH); 7.22 − 6.51 (m, 3H, ArH); 4.82–4.41 (m, 0.982 H, C$\underline{H}_2$-C≡CH); 4.05–3.52 (2.52 H, m, -CH$_2$-C≡C$\underline{H}$ and m, -CH$_2$-).

APN-25: ^{1}H-NMR (600 MHz, δ, ppm, DMSO-d6): 9.28 (br.s., 1.21 H, -OH); 7.24 − 6.57 (m, 3H, ArH); 6.04–5.75 (m, 0.19 H, CH$_2$-C$\underline{H}$=CH$_2$), 5.42–4.91 (m, 0.37 H, CH$_2$-CH=C$\underline{H}_2$), 4.83–4.54 (m, 0.46 H, C$\underline{H}_2$-C≡CH); 4.42–4.16 (m, 0.38 H, C$\underline{H}_2$-CH=CH$_2$); 4.09–3.53 (2.2 H, m, -CH$_2$-C≡C$\underline{H}$ and m, -CH$_2$-).

APN-10: ^{1}H-NMR (600 MHz, δ, ppm, DMSO-d6): 9.27 (br.s., 1.08 H, -OH); 7.22 − 6.51 (m, 3H, ArH); 6.02–5.73 (m, 0.35 H, CH$_2$-C$\underline{H}$=CH$_2$), 5.43–4.94 (m, 0.71 H, CH$_2$-CH=C$\underline{H}_2$), 4.88–4.50 (m, 0.17 H, CH$_2$-C≡CH); 4.41–4.11 (m, 0.69 H, C$\underline{H}_2$-CH=CH$_2$); 4.03–3.50 (2.08 H, m, -CH$_2$-C≡C$\underline{H}$ and m, -CH$_2$-).

2.4. Washing resins from potassium ions

To the portion of 50 g of resin after synthesis 200 ml CH$_2$Cl$_2$ was added at 40 °C. After complete resin dissolution, the solution was washed twice with 200 ml of 5% aqueous acetic acid and 200 ml of water in a separating funnel. The solvent was removed by a rotary evaporator. No significant changes in the NMR spectra of the washed and unwashed resins were observed.
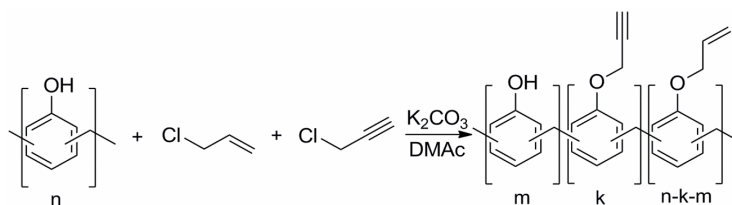
Fig. 1. Alkylation of novolac resin by Williamson reaction.

2.4.1. Determination of potassium ions content in resins

The content of potassium ions in the resin was determined by ion chromatography of the dry residue after the combustion of the obtained resins at 900 °C. The entire dry residue was K_2CO_3. The dry residues were weighed then dissolved in water and the concentration of potassium ions in all solutions was analyzed with a 930 Compact IC Flex ion chromatography system (Metrohm, Switzerland) with a Metrosep C 4 column (150×4×4 mm, Metrohm, Switzerland).

2.5. Volumetric shrinkage

During curing, the samples decreased in size (shrinkage) as a result of the formation of a three-dimensional polymer network. The volumetric shrinkages were determined by density change before ($\rho_{uncured}$) and after polymerization (ρ_{cured}) of resins according to Eq. (1) [19,20].

$$\frac{\Delta V}{V_0} = \frac{V_0 - V_1}{V_0} = \frac{\rho_{uncured}}{\rho_{cured} - \rho_{uncured}} \qquad (1)$$

where V_0 is the original volume and V_1 is the volume after shrinkage.

The hydrostatic weighing technique was used to determine densities. It is a regular density measurement technique according to which the weight W of a sample is measured in two different conditions, in our case water and air. The density is calculated from [21]:

$$\rho = \frac{W_{air}\rho_w}{W_{air} - W_W} \qquad (2)$$

where ρ is the density of the sample, W_{air} is weight of the sample in air, W_w is the weight of the sample underwater, ρ_w is the density of water.

2.6. CFRP manufacturing

CFRPs were obtained with dimensions of 500×700×4 mm by a vacuum infusion process on stainless steel plate coated with release agent. Fluoroplastic tubes for resin feeding and vacuum channels were placed in front of each of the plate's sides. The sealing tape was formed along the perimeter of the steel plate. Under the feeding channel, 10 layers of carbon fabric (330×330 mm, 200 g/m²) was placed. After that, the carbon fabric was covered with a distribution medium and a peel ply. Finally, a vacuum film was attached to the perimeter of the plate using a sealing tape. Further, the vacuum bag was connected through a vacuum channel to the vacuum pump, placed in the oven, and heated to the desirable temperature. The preheated resin was infused through a feed channel only after reaching 1 kPa inside the vacuum bag. Impregnation was ended after 20–30 min then the resin appeared in the vacuum channel. After the infusion process, curing was carried out at 180 °C for 8 h. After that, the vacuum bag was disassembled, and the cured sample was post-cured according to the following temperature program: 200 °C – 3 h, 220 °C – 3 h, 250 °C – 2 h, 300 °C – 1 h.

3. Result and discussion

3.1. The synthesis and viscosity characterization of modified resins

In this work, novolacs modified by propargyl or both propargyl and allyl groups with a total substitution of 50% were investigated as matrices for CFRP obtained by vacuum infusion (Table 1) [18]. They were synthesized according to the Williamson reaction as described in the previous work (1) [18, 21].

All the obtained resins showed a viscosity of about 1000 mPa·s at 140 °C (Table 2). At the same time, due to incomplete substitution of OH-groups, bound potassium ions can remain in the resins. Contents of potassium ions in resins were investigated by ion chromatography analysis of the dry residue after the process of pyrolysis. It is assumed that the formation of linear polymer conformations due to electrostatic inhibition of rotation around the methylene bridges by the negatively charged phenolates leads to a significant increase in viscosity as compared to the neutral form of OH-groups (Fig. 2) [22, 23].

Table 1
Thermal and mechanical properties of alkylated novolac resins [18]

Resin	Allyl/propargyl ether content, %	T_{hd}, °C	Y_c at 980 °C, Ar, %	$T_{5\%}$, °C	Flexural strength, MPa	Flexural modulus, GPa
APN-10	35/9	271	45.4	410	143	5.6
APN-25	23/18	255	49.6	406	106	6.2
PN-50	0/49	214	59.6	410	101	6.5

T_{hd} – heat deflection temperature; Y_c – char yield; $T_{5\%}$ – temperature at 5% weight loss.

Table 2
Viscosity characteristics of investigated resins

Resin	K^+ content, %	Viscosity, mPa·s, at 140 °C	Viscosity, mPa·s, at 160 °C	k_η at 160 °C, h^{-1}
PN-50	5.6	901	562	0.84
	0.6	625	367	0.45
APN-25	5.2	897	501	0.67
	0.4	412	251	0.34
APN-10	6.1	1112	512	0.42
	0.4	517	312	0.2

It is shown by dynamic viscosity and isothermal viscosity tests (Fig. 3) of resins that potassium ions remaining in the resin after synthesis indeed increase their melt viscosity (Table 2). To eliminate ions K^+ off the resins, they were washed in a 5% acetic acid solution after the synthesis, as was described in the experimental section. The acid reacts with phenolates to form a neutral form of phenol-formaldehyde resin and potassium salt. Washing of the resins indeed results in a significant reduction of viscosity.

To assess the dynamics of the viscosity change after washing the resin, a "viscometric" kinetic constant was used. An exponential equation characterizes viscosity growth in all the investigated resins curing at 140 and 160 °C and can be described with a "viscometric" kinetic constant, k_η [24].

$$\eta = \eta_0 \, exp(k_\eta t) \qquad (3)$$

where η_0 is the initial viscosity (mPa·s); k_η is the viscosity kinetic constant (h^{-1}).

The values of the rate constants for the increase in viscosity (see Table 2) were determined by a graphical method with the use of Eq. (3) in semi-logarithmic coordinates:

$$ln(\eta) = ln(\eta_0) + k_\eta t \qquad (4)$$

In the case of the utilization of common auxiliary materials, the vacuum infusion process has to be performed at temperatures not higher than 180–200 °C. At the same time, the infused resin must have a viscosity lower than 800 mPa·s at the processing temperature for the impregnation of reinforcing fibers [25]. The results of the viscosity analysis show the possibility of obtaining composites by vacuum infusion at 140–160 °C only for the following resins PN-50, APN-25, APN-10, that are washed when the K+ ion content is less than 0.6%.
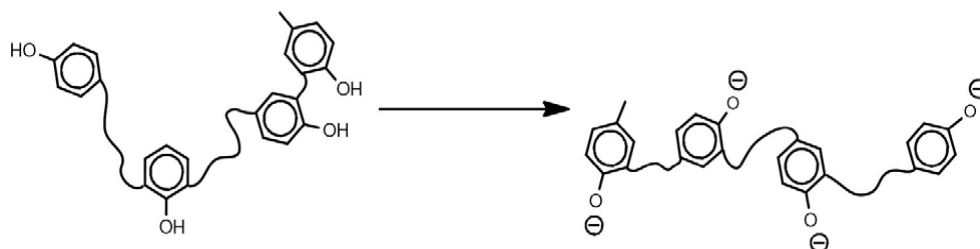
Fig. 2. The supposed mechanism of increasing viscosity of resins in the presence of potassium ions.
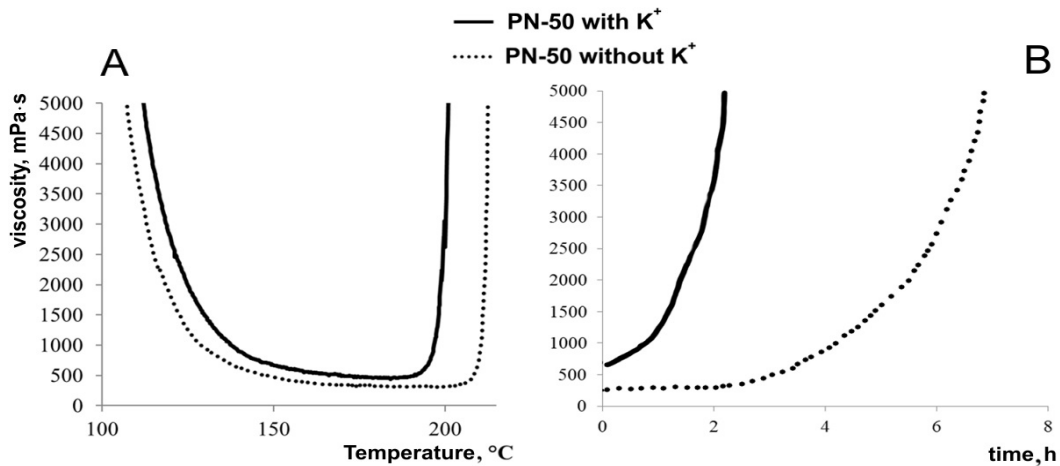
Fig. 3. Viscosity profile (A) and isotherm (160 °C) (B).

For unwashed resins, the viscosity at 140 °C significantly exceeds the maximal viscosity required for vacuum infusion (800 mPa · s), and at 160 °C the resin's gelation rate is too fast. The rate of gelation increases with the increase of the content of propargyl groups (from APN-10 to PN-50) which is due to the polymerization of chromene fragments at 160 °C (Fig. 4). Chromene fragments are formed after the Claisen rearrangement of propargyl groups[26, 27]. At higher temperatures, the polymerization of the resin causes a rapid increase in its viscosity, which prevents the impregnation of reinforcing fibers.
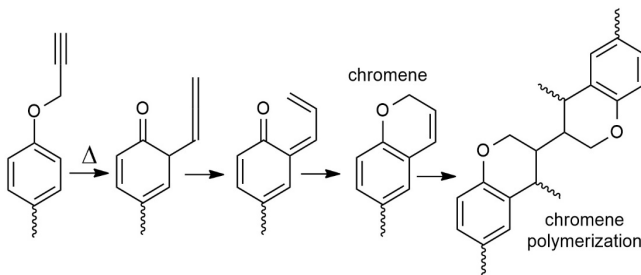
Fig. 4. Mechanism of the chromene fragments formation and their polymerization reaction.

3.2. Mechanical properties of composites

CFRP with standard carbon fabric was manufactured by vacuum infusion with a matrix content of 35–37 %. According to the viscosity analysis of investigated resins, vacuum infusion was performed at a temperature of 140 °C for about 30 min. After the infusion process had been completed, the infusion system was placed in the oven at 180 °C for 8 h. The system was disassembled and post-cured. High-performance CFRPs were obtained with a matrix content of 35–37%. Mechanical properties were investigated for all the obtained composites (Table 3).

For the neat cured resins, the best mechanical properties are observed for PN-50 with the highest content of propargyl groups (flexural modulus = 6.5 MPa) [18]. Therefore, it was expected that CFRP with the matrix from this resin would show the best mechanical properties. However, from the data shown in Table 2, it is clear that CFRP with APN-25 matrix has the best properties.

To explain this relationship, the shrinkage of the resin during the curing process was examined. The densities of cured and uncured samples were

Table 3
Mechanical properties of the CFRP samples at 25 °C

Resin matrix	Compressive		Tensile		In plane shear strength, τ_{12}, MPa	Interlaminar shear strength, τ_{13}, MPa
	$\sigma_{11}-$, MPa	E, GPa	$\sigma_{11}+$, MPa	E, GPa		
PN-50	398.2 ±11.2	63.0±0.7	674.2±11.2	63.3±1.9	80.8±2.1	31.8±1.9
APN-25	521.7±11.1	62.7±1.11	748.6±10.3	67.2±2.1	82.94±1.2	43.6±2.1
APN-10	413.3±21.1	53.1±2.3	727.5±26.8	55.8±1.8	70.91±3.2	24.9±2.1
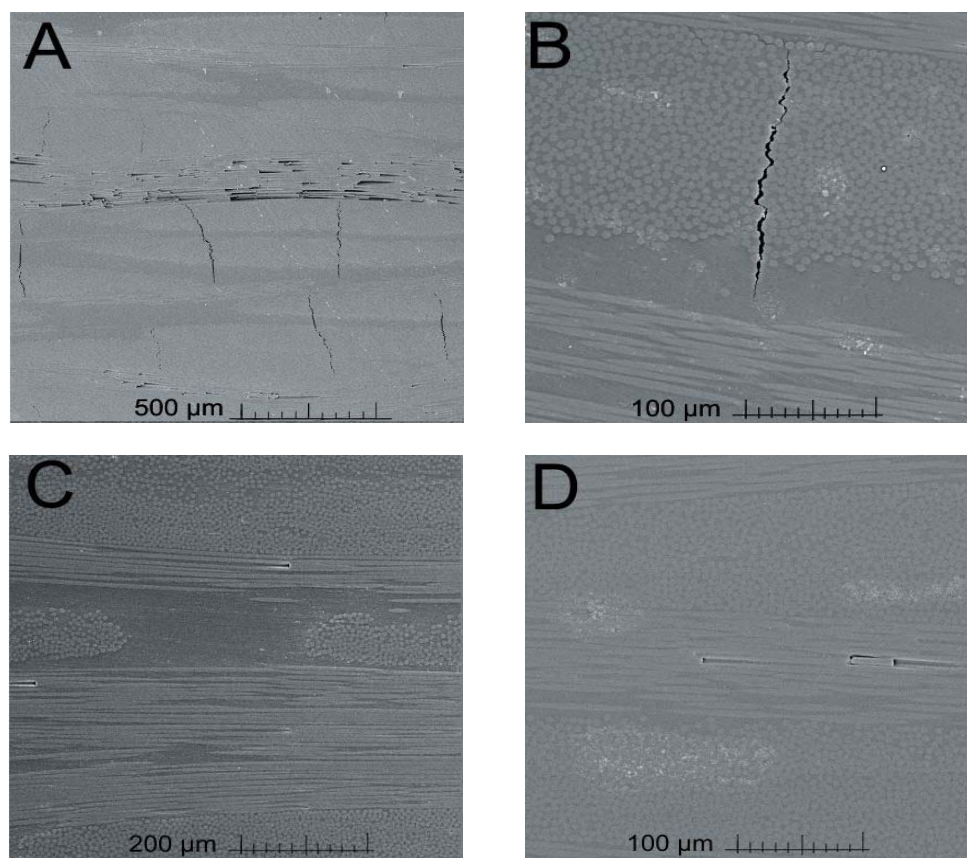
Fig. 5. SEM images of CFRP microcracking based on APN-10 resin (A, on a larger scale - B) and the absence of microcracking in CFRP based on APN-25 (C) and PN-50 (D) resins.

measured, and it showed that APN-10 resin was characterized by the highest volume shrinkage, about 3% (PN-50 (0.5%), APN-25 (1.4%)), which is also reflected in the SEM images: for APN-10 based CFRP characteristic microcracking is observed at an angle of 90° to the direction of the fibers [28] for PN-50 and for APN-25 microcracking is not observed (Fig. 5).

The shear strength test at elevated temperatures was used to estimate the thermal behaviour of the composites (Table 4). The composites retain up to 94–96% of in plane shear strength at 200 °C and 50–70% at 230 °C. Mechanical properties decrease with temperature growth more sufficiently for the samples with a high content of propargyl groups in the resin. These data are in accordance with DMA analysis of investigated resins (Fig. 6). Storage modulus decreases more rapidly with increasing temperature for the resin PN-50. Glass transition temperatures which were observed around 215–270 °C increase with the increasing of allyl groups content in the resin.

Table 4
Mechanical properties of the composites at elevated temperatures

Resin matrix	Temperature, °C	In plane shear strength, τ_{12}, MPa	Retention of plane shear strength,	Inter laminar shear strength, τ_{13}, MPa	Retention of laminar shear strength, %
PN-50	200 °C	76.1±3.9	95	31±2.3	99
	230 °C	30.5±3.1	37	17.3±2.6	54
APN-25	200 °C	80.7±2.5	96	41.8±1.5	95
	230 °C	61.2±1.1	74	30.6±1.1	71
APN-10	200 °C	61.4±2.1	82	23.8±3.1	96
	230 °C	47.1±1.6	66	18.8±1.0	76

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