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Propargylated Novolac Resins for Solvent-Free Technology for High-Performance Composites

D. Kalugin[1*], S. Nechausov[1], A. Galiguzov[1], A. Malakho[1], V. Lepin[2], L. Oktiabrskaia[2], S. Minchuk[2]

[1]M.V. Lomonosov Moscow State University, Department of Chemistry, Leninskie gory 1-3, 119234, Moscow, Russia
[2]JSC SPLAV, Scheglovskaya zaseka st, 33, Tula Region, 300004, Tula, Russia

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Abstract

Propargyl substituted novolac phenolic resin diluted with unsaturated bisphenol-A ethers was used for glass fiber solvent-free impregnation for the formation of high-performance composites. The addition of 20% mass of diallyl (DAEBA) or dipropargyl (DPEBA) bisphenol-A to propargyl substituted novolac phenolic resin resulted in viscosity drop from 2000 mPa·s to 400–500 mPa·s at 140 °C. This proved to be enough to achieve complete impregnation of the twisted glass fibers, as illustrated by SEM analysis. This improvement in impregnation was shown to result in increasing both flexural strength and modulus of the unidirectional glass fiber composite material approximately with a factor of two compared to the composite impregnated with resin without bisphenol-A ethers. DPEBA was shown to be more suitable for high-temperate applications since its addition does not seem to result in a decrease of the heat deflection temperature (HDT).

1. Introduction

Phenolic resins are well-known as materials of high heat resistance, low coefficient of thermal expansion (low CTE), good fire resistance and are applied as matrices for composites with carbon, basalt, glass et al. [1] Among the disadvantages that limit their application in high-performance composites, phenolic resins require solvent technology for their impregnation, especially when twisted yarns are considered. This requirement is due to the high viscosity of phenolic resins melts and curing reactions that occur during heating. The first issue could be solved by using “active diluents” that are successfully implemented in other resin systems. The second one demands modifications of the phenolic resin in order to change the curing mechanism. It is known that the introduction of allyl, [2–4] propargyl, [5–7] maleimide, [4, 8] phenylethinyl [9] etc. increases heat and thermooxidation resistance and changes the curing process to an addition type reaction. The advantages of this approach include low cost and a simple synthesis procedure of the target material. Propargylated novolac resins (PN) are known to possess an increased thermal stability and char yield as compared with other types of modified phenolic resins. [5, 10] This modification results in a curing onset temperature shift up to 200 °C and a curing peak up to 250 °C, thus making these resins attractive for solvent free technology for high-performance composites applications.

In this study PN resins with active diluents based on bisphenol-A unsaturated ethers are used for the solvent-free impregnation of twisted glass fibers for the formation of high-temperature resistant composites. PN resins can thus be used as a component of the polymer matrix for composite valves for high-temperature applications.

2. Experimental

2.1. Materials and methods

Novolac resin (Metadynea) 99.7% purity, propargyl chloride 98% purity(Aldrich), allyl chloride 98% purity (Aldrich), DAEBA technical grade (Aldrich) were used without purification.

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*Corresponding author. E-mail: kalugin_denis@mail.ru

Twisted glass fiber yarn (Polotsk) was used as received.

(3-Glycidyloxypropyl) trimethoxysilane 98% purity (Aldrich) was used without purification.

^{1}H NMR spectra were measured on a Bruker Avance 600 instrument operating at a frequency of 600 MHz. Chemical shifts in ^{1}H NMR spectra (ppm) were presented on the δ scale relative to tetramethylsilane.

Thermal stability was evaluated by TGA (Thermogravimetric analysis) on a Netzsch TG 209 P3 Tarsus apparatus, at a heating rate of 10 °C/min in range 40–980 °C and an Ar purge rate of 50 mL/min.

Flexural test was carried out on Tinius Olsen H100KS testing machine.

Heat deflection temperature was measured by the 3-point bending method according to ASTM-E2092-03 on a Netzsch TMA 402 with 1.82 MPa loading.

Resins viscosities and processing times were determined with a Brookfield CAP 2000+ Viscometer using cone №10 at 40 RPM.

SEM analysis was carried out using a scanning electron microscope TESCAN VEGA3 LMU at an accelerating voltage of 20 kV.

2. Resins synthesis

2.1. PN-50 resin synthesis

Propargylated novolac resin with 50% (PN-50) substitution degree was synthesized according to Scheme 1.

37.7 g (0.35 moles) of novolac resin was placed in a 250 ml one-neck flask equipped with a reflux condenser and dissolved in 100 ml of DMAc (dimethyl acetamide). Then 31.0 g of powdered K_2CO_3 (0.224 moles) was added. After that, propargyl chloride (13.1 g, 0.175 moles) was added gradually during 20 min. The reaction mixture was heated to 60 °C and stirred overnight. Then it was separated from the solids and the solvent was removed on a rotary evaporator. The residue was dissolved in DCM (dichloromethane) (200 ml) and washed with 1% s acetic acid water solution (3×100 ml) and then with brine (5×100 ml). The solvent was removed and the resin was dried under reduced pressure. (1 mm Hg, 100 °C, 4 h). Dark solid resin was obtained. ^{1}H-NMR (600 MHz, $(CH_3)_2SO$, δ, ppm) (δ, ppm): 9.32 (br.s., -OH); 7.2–6.5 (m, ^{3}H, ArH); 4.8–4.3 (m, 1.38 H, OCH_2); 4.0–3.4 (m, 2.66 H, $-CH_2-$, $C{\equiv}CH$).

2.2. DPEBA synthesis

Dipropargyl bisphenol-A was synthesized according to Scheme 2.

79.9 g (0.35 moles) of bisphenol A was placed in a 500 ml one-neck flask equipped with a reflux condenser and dissolved in 250 ml of DMAc. Then 62.0 g of powdered K_2CO_3 (0.448 moles) was added. After that, propargyl chloride (26.2 g, 0.35 moles) was added gradually during 20 min. The reaction mixture was heated to 60 °C and stirred overnight. Then it was separated from the solids and the solvent was removed on a rotary evaporator. The residue was solved in DCM (300 ml) and washed with 1% s acetic acid water solution (3×100 ml) and then with brine (5×100 ml). The solvent was removed and the product was dried under reduced pressure. (1 mm Hg, 100 °C, 4 h). Pale-yellow crystalline monomer was obtained (yield 86%). ^{1}H-NMR (600 MHz, $CDCl_3$, δ, ppm): 7.2–6.5 (m, 8H, ArH); 4.43 (d, 4H, $-CH_2-C{\equiv}CH$), 2.48 (t, 2H, $-CH_2-C{\equiv}CH$); 1.64 (s, 6H, $(CH_3)_2CAr_2$).

2.3. Composites preparation

2.3.1. Impregnation

2.3.1.1. Solvent free impregnation

Twisted glass fiber was coated with (3-Glycidyloxypropyl) trimethoxysilane and pulled through the resin (PN-50; PN-50 with 20% mass. DAEBA and PN-50 with 20% mass. DPEBA) melt at 125 °C. The surplus resin was removed by pulling through a spinneret heated at 125 °C with a hole diameter of 300 μm as shown on Fig. 1. The final resin content is about 30% mass. The corresponding samples are named S1, S2 and S3.

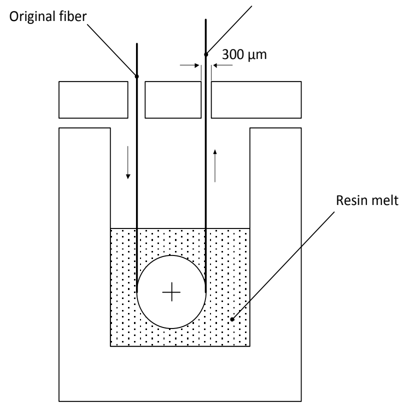
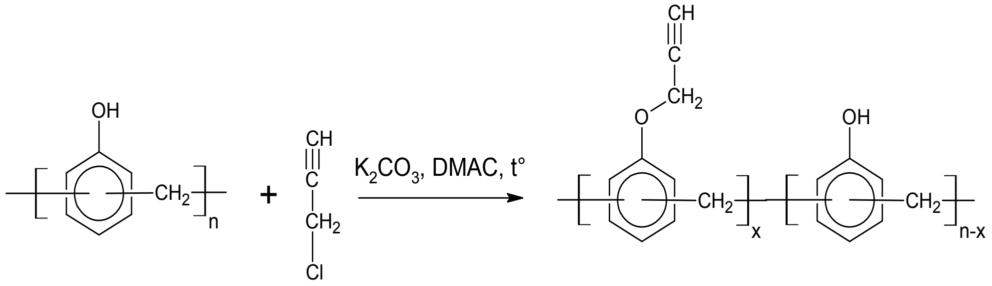
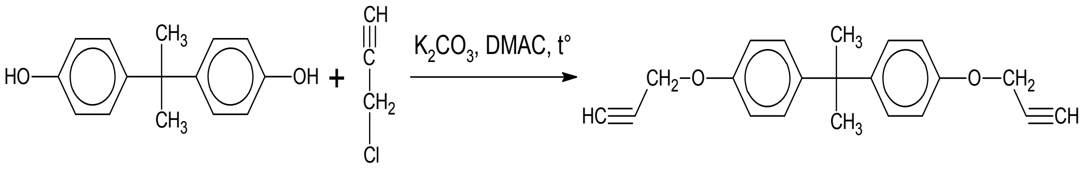


Fig. 1. Principal scheme of solvent free impregnation process.



Scheme 1. PN-50 synthesis scheme by Williamson reaction.



Scheme 2. DPEBA synthesis scheme by Williamson reaction.

2.3.1.2. Solvent impregnation

A twisted glass fiber was pulled through 40% solution of PN-50 resin in acetone. Impregnated fibers were dried at 100 °C for 12 h. The final resin content after drying is about 30%. The corresponding sample is named S4.

2.3.2. Composites hot pressing

Unidirectional composites were pressed at 200 °C and 20 MPa load with post-cure at 250 °C for 4 h.

3. Results and Discussion

3.1. Synthesis

According to our previous paper [11] novolac resin with 50% substitution degree (PN-50) possesses optimal thermal characteristics for composites preparation and thus was selected for investigation in the current research.

3.2. Thermal properties of the synthesized resins

The heat resistance study of the cured resins was performed by TGA in argon atmosphere. The results are shown in Table 1.

One can see that DPEBA possesses both increased thermal stability ($T_{5\%}$) and higher char yield (Y_c) in comparison with DAEBA. This makes propargyl substituted bisphenol-A (DPEBA) more attractive as a diluent for PN-50 resin, considering its thermal properties.

Table 1
Thermal properties of the cured resins

Resin	$T_{5\%}$, °C	Y_c at 900 °C, %
PN-50	410	65
DAEBA	310	23.5
DPEBA	400	41

3.3. PN-50 resin mixtures with bisphenol-A ethers

3.3.1. Viscosity

To investigate the influence of active diluents on resin properties, mixtures of PN-50 resin with DAEBA and DPEBA as active diluents were prepared. The results of the viscosity measurements are shown on Figs. 2 and 3 correspondingly.

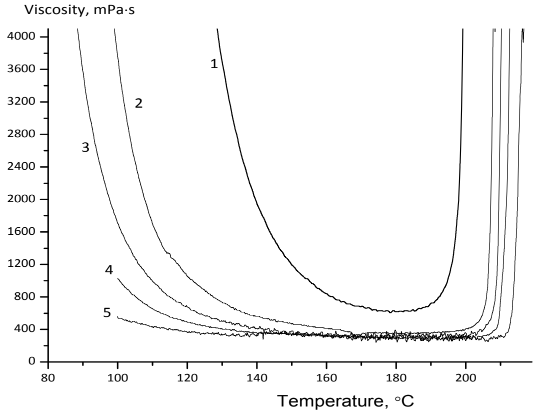


Fig. 2. Viscosity-temperature plots for PN-50 resin/DAEBA mixtures with various DAEBA content (mass.%): 0% (1); 10% (2); 20% (3); 33% (4); 50% (5).

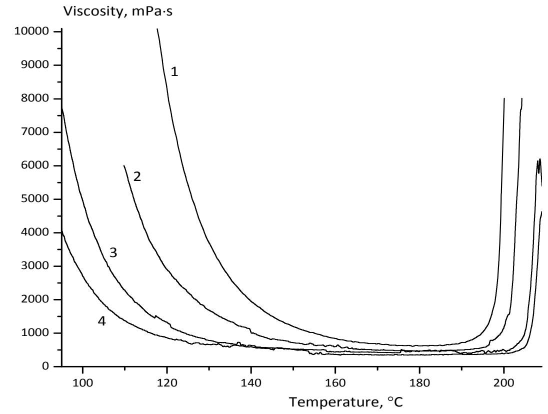


Fig. 3. Viscosity-temperature plots curves for PN-50 resin/DPEBA mixtures with various DPEBA content (mass.%): 0% (1); 20% (2); 33% (3); 50% (4).

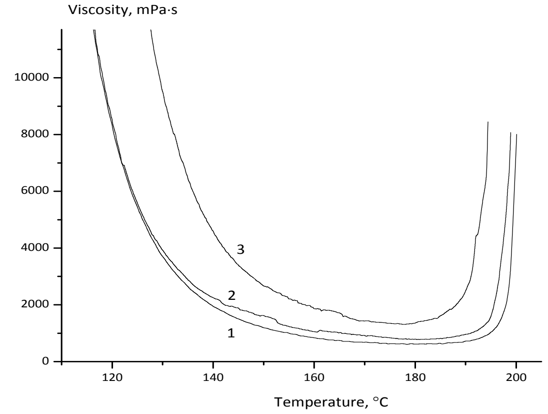


Fig. 4. Viscosity-temperature plots for PN-50 resin: untreated (1); heated for 3 h in vacuum (2); heated for 3 h in air (3).

One can see that DAEBA is a more effective viscosity reducer up to 150–160 °C than DPEBA. The effect of diluent addition is levels off at temperatures higher than 160 °C.

It should be pointed out that heating in air at a temperature of 140 °C results in a viscosity increase, unlike heating in vacuum (see Fig. 4). The viscosity increase for the treatment in air is likely related to oxidation reactions and limits the time and temperature of the impregnation process.

Thus DAEBA is more suitable for preparing composites when a low viscosity is strongly required, e.g. in infusion, RTM (Resin Transfer Molding) and similar processes.

3.3.2. Thermal properties

The results of the TGA analysis for mixtures of PN-50 resin with DAEBA and DPEBA are shown on Figs. 5 and 6 respectively.

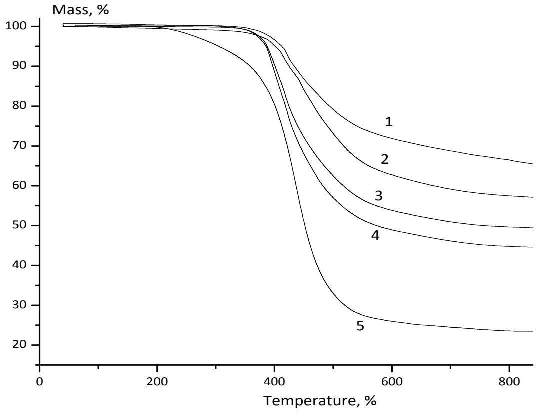


Fig. 5. TGA curves for cured PN-50 resin/DAEBA mixtures with various DAEBA content (mass.%): 0% (1); 10% (2); 33% (3); 50% (4); 100% (5).

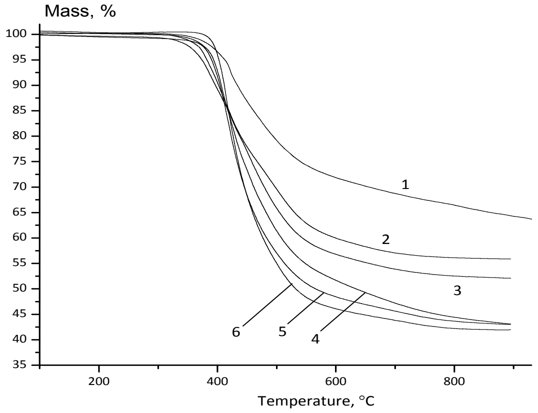


Fig. 6. TGA curves for cured PN-50 resin/DPEBA mixtures with various DPEBA content (mass.%): 0% (1); 10% (2); 20% (3); 33% (4); 50% (5); 100% (6).

One can see that both DAEBA and DPEBA addition results in a decrease in char yield, but does not significantly reduce the decomposition temperature, notwithstanding the fact that DAEBA possesses a reduced thermal stability (curve 5, Fig. 5). The reason for this increased thermal stability of PN-50/DAEBA mixtures in comparison with the original cured DAEBA could be explained by the integration of allyl units into the propargyl network. It should also be pointed out that the influence of DPEBA addition on the char yield is considerably different from the one for DAEBA.

The char yield for cured PN-50 resin/DAEBA mixtures could be calculated by the following equation:

$$Y_C^{calc} = Y_C^{DAEBA} \cdot x_{DAEBA} + Y_C^{PN-50} \cdot (1 - x_{DAEBA})$$

where: Y_C^{calc} – calculated char yield of the resulted mixture; x_{DAEBA} – content of DAEBA, mass.%;

Y_C^{PN-50} – char yield of the PN-50 resin; Y_C^{DAEBA} – char yield of the cured DAEBA.

But the PN-50/DPEBA mixtures do not fit this equation.

The summarized data for mixtures of PN-50 resin with DAEBA and DPEBA are presented in Table 2.

Table 2
Char yields for cured mixtures of PN-50 resin with DAEBA and DPEBA

Diluent content, mass.%	DAEBA		DPEBA	
	Y_C, %	Y_C^{calc}, %	Y_C, %	Y_C^{calc}, %
0	65	65	65	65
10	57	60.9	56	62.6
20	55	56.7	52.3	60.2
33	50	51.3	43	57.1
50	44.6	44.3	43	53
100	23.5	23.5	41	41

The peculiarities of the influence of the DPEBA addition on the char yield is not clear yet and further investigations are required.

The opposite situation occurs when considering the heat deflection temperature (HDT) of the corresponding mixtures. The addition of DAEBA to PN-50 resin results in a decrease of the HDT of the cured PN-50/DAEBA mixture, whereas DPEBA does not exert any influence (Table 3).

Thus DPEBA is the more attractive diluent agent when taking the final properties into account, but the high viscosity of its blends with PN-50 resin could limit its application.

Table 3
HDT values of cured resins

Diluent	HDT, °C
none	250
DAEBA (20% mass.)	155
DPEBA (20% mass.)	254

3.4. Composites properties

Despite the higher viscosities of the PN-50/DPEBA blends in comparison with the PN-50/DAEBA ones, both systems provide a complete impregnation according to the SEM analysis (see Figs. 8 and 9). On the contrary, one can see that there are areas of non-impregnated fibers in the composite based on pure PN-50 without diluent addition (see Fig.7).

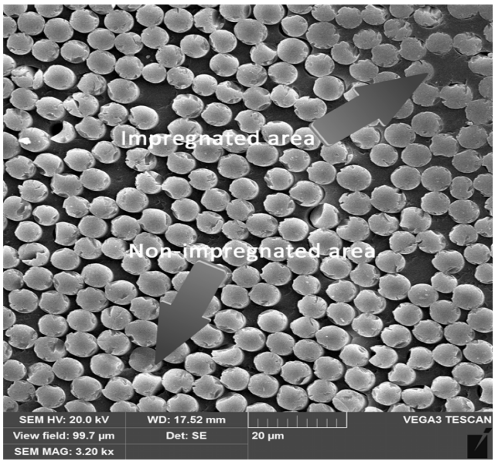


Fig. 7. Cross-section of composite obtained via solvent-free impregnation without diluent.

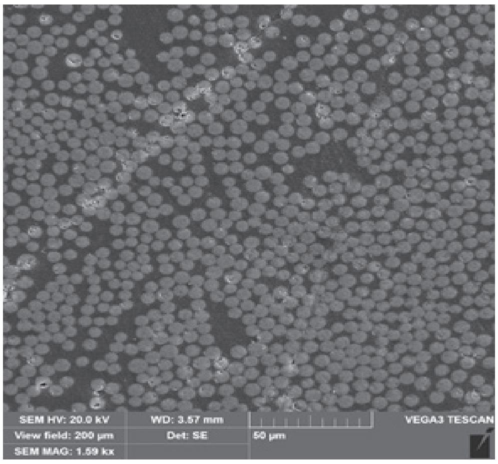


Fig. 8. Cross-section of composite obtained via solvent-free impregnation with DAEBA as diluent.

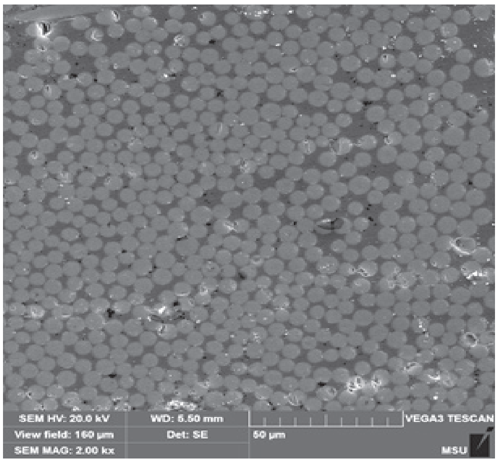


Fig. 9. Cross-section of composite obtained via solvent-free impregnation with DPEBA as diluent.

This difference in impregnation quality results in a significant difference in mechanical properties (see Table 4) of the unidirectional glass fiber composites.

Table 4
Mechanical properties of unidirectional glass fiber composites

Sample	Diluent	Flexural properties	
		σ_{flex}, MPa	E_{flex}, GPa
S1	no diluent	410	15
S2	DAEBA	726	24
S3	DPEBA	731	28
S4	Acetone	590	25

Both σ_{flex} and E_{flex} increase approximately twice for samples S2 and S3 in comparison with specimen obtained by impregnation without any diluent (S1). It should be pointed out that composite sample S4, obtained by impregnation with 40% mass. acetone solution (i.e. an ideal impregnation), has approximately the same mechanical properties as samples S2 and S3.

4. Conclusions

The application of propargylated novolac resin for a solvent free impregnation process is investigated. Composites obtained by impregnation of twisted glass fiber with melted PN-50 resin showed reduced mechanical properties due to an incomplete impregnation as proved by SEM analysis. When adding either DAEBA or DPEBA to PN-50 resin, the melt viscosity is reduced and a complete impregnation is obtained. The latter results in an improvement of the mechanical characteristics. At the same time DPEBA was shown to be a more suitable additive for high-performance composites since a DPEBA addition does not result in decrease of the HDT.

Acknowledgements

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