Dual-Cure Propargyl Novolac-Epoxy Resins: Synthesis and Properties

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SUMMARY
A partially propargylated oligomeric phenolic novolac (PPN) was synthesised by the Williamson’s reaction of a novolac with propargyl bromide and was characterised. Reactive blending of the PPN resin with epoxy resin resulted in a dual cure thermoset. The curing occurred through the phenol-epoxy reaction at about 135°C together with a Claisen rearrangement and the addition polymerisation of propargyl ether groups at around 235°C. The phenol-epoxy reaction could be catalysed by triphenyl phosphine, without affecting the curing of the propargyl ether groups. The cure characterisation was done by DSC and DMA. The effect of the phenol-epoxy ratio on the adhesive properties of the PPN-epoxy blend between aluminium adherends was evaluated. The system exhibited moderately good lap shear strength which was optimised for a phenol:epoxy equivalent ratio of 2:1. Good retention of the properties was observed at 100°C. On a comparative scale, the diglycidyl ether of bisphenol-A was better than the novolac epoxy, in improving the adhesion. Addition of conventional matrix tougheners was not conducive to improved adhesion. The system formed a good composite with glass fabric. The mechanical properties of the glass laminates were independent of the phenol-epoxy stoichiometry. The cured system possessed good thermal stability and a Tg>300°C. The epoxy adversely affected the Tg and the thermal stability.

INTRODUCTION
Propargyl ether-functional phenolic resins are known to be potential hydrophobic substitutes for epoxies in advanced composites, electronics, adhesives and coatings. The structural similarity of propargyl ether to epoxy resins is useful for the preparation, processing and development of thermally stable polymers. The synthesis and curing of bispropargyl ether resins (BER) based on diphenols is quite well documented1-4. They are moderately thermally stable systems with properties comparable to the epoxies. The curing of propargyl ether resins proceeds by the Claisen rearrangement followed by the addition polymerisation of the resultant chromene5. The structural dependence on cure kinetics of BER has also been investigated6. Propargyl-novolac (PN)resins formed from novolacs are more thermally stable but there are only a very few reports of their synthesis and properties7. In earlier work, we reported the synthesis and properties of high molar mass PN resins8.

Their thermal stability was dependent on the degree of substitution of propargyl groups9. The highly exothermic curing reaction (ΔH~1200 J/g) was effected at temperatures above 200°C, and this often posed problems in their processing, caused by resin bleeding at the high temperature. The hydrophobic nature of completely propargylated novolac may be undesirable for composites. One way to obviate these problems may be to induce partial curing of the PN resins at a relatively low temperature, preferably through a mechanism other than propargyl curing.

From this perspective, we have designed a dual-cure system based on partially propargylated novolac (PPN) through its reactive blending with epoxy resins.
The strategy is to induce gelation at a lower temperature through the phenol-epoxy reaction. There are a few reports on the blends and structural modifications of propargyl novolac (PN) resins. Thus, the adhesive strength of phenol-formaldehyde resin is reported to be increased by modification with propargyl glycidyl ether. Thermosetting resins with good dimensional stability and heat resistance have been claimed on mixing propargyl-etherified resin with resole. Laminating resin compositions with good workability and curability, having heat and moisture resistance and a low dielectric constant, are obtained by using propargyl-etherified phenolic resin-based formulations. Propargyl ether-terminated ester-imide prepolymers and benzoxazine monomers containing propargyl ether groups have also been also reported.

This paper reports the synthesis of PPN resin, its reactive blending with epoxy resin, its cure characterisation and some properties of the cured systems. The effect of phenol-epoxy stoichiometry on the properties of the polymer is examined.

EXPERIMENTAL

A. Materials

Phenol (CDH, Agra, India), formalin (34% solution, Qualigens, India), oxalic acid (NICE, India) and propargyl bromide (3-bromo, 1-propyne, ACROS, Belgium) were used as received. Other solvents were also used as received. Silane treated, plain weave E-glass of thickness 0.175 mm and 8 harness satin weave was received from Unnathi Corporation, India and was used as reinforcement. The precursor novolac was synthesised by reacting phenol with formaldehyde in the presence of oxalic acid at 90°C. To a mixture of phenol (500 g) and oxalic acid (25 g), formaldehyde (289 cm³ of 34% aqueous solution) was added drop-wise while the system was heated in an oil bath at 80°C under agitation. After the addition, the temperature was raised and maintained at 90°C for 8 h. On completion of the reaction, the product was washed with hot distilled water to remove the unreacted phenol. The resin was mixed with 500 cm³ toluene and then subjected to Dean and Stark distillation to remove the water. Toluene was decanted and the resin was dried in vacuum at 60°C for 4 h. Yield was 330 g.

D. Synthesis of Novolac–Propargyl Ether Resins

200 g novolac was dissolved in 600 cm³ AR acetone. 350 g dried, powdered potassium carbonate and 5 g benzyl triethylammonium chloride were added. Propargyl bromide (133 cm³ 80% solution in toluene) was then added drop-wise at 60°C under agitation. The system was kept agitated for 35 h at 60°C. The mixture was filtered and the filtrate added to cold water to precipitate the resin. It was dissolved in acetone and reprecipitated in water. After decantation of water, the resin was dried by flash evaporation under vacuum at 60°C. It was characterised by GPC and hydroxyl value. Further characterisation was done by FT-IR.

E. Thermal Curing

Curing of the propargylated novolacs (neat castings) was effected by heating slowly in a programmed manner in an air oven from ambient to 220°C and maintaining at that temperature for 120 min. The cure schedule is given below. The completion of cure was monitored by FT-IR. It was also ascertained by DMA.
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Temp (°C) 100 125 150 175 200 220
Hold Time (min.) 30 30 60 30 30 120

F. Preparation of Composites

Glass fabric was impregnated with a solution of the resin blend in methyl ethyl ketone (MEK) and dried at room temperature for about 18 h. The prepregs were then cut into pieces of dimensions 12 cm x 10 cm, stacked and moulded in a hydraulic press between thick metallic platens to achieve the proper number of plies and correct thickness. Laminate composites of dimensions 10 cm x 12 cm x 0.5 cm were prepared according to the above cure schedule. A pressure of 1.5 MPa was applied at 140°C after gelation.

G. Composite Testing

The mechanical testing of the composites was performed as per the following ASTM procedures using an Instron UTM model 4202.

Interlaminar Shear Strength (ILSS):
ASTM D 2344 – ’76 (vol.36, 1982)
Flexural Strength:
ASTM D- 790-’81 (vol. 35, 1982)
0° Compressive Strength:
ASTM D-3410-75 (vol. 35,1982)

H. Adhesive Properties

Lap shear strength (LSS) was determined as per ASTM D-1002, using chromic acid etched, B-51-SWP aluminium as the substrate. A 25% solution in MEK of the blend of PPN and epoxy containing 1 wt.% of triphenyl phosphine (TPP) was uniformly applied as a thin layer over the aluminium substrate. The solvent was allowed to evaporate by keeping the specimens in a hot air oven at 75-80°C for about 2 h. They were then allowed to cool to room temperature and assembled together for testing the adhesive properties. Curing at the desired temperature was carried out in a hot air oven and a pressure of nearly 0.5 MPa was applied over the bonded specimens using the lever-press assembly. The bonded specimens were tested in an Instron UTM Model 4202, at a cross head speed of 10 mm/min. For determining the LSS at 100°C, the specimens were soaked for 10 min and then tested at that temperature.

In the case of thermoplastic modified formulations, a 10 weight% solution of the blend of PPN and EPN and thermoplastic (PS or PC) in dichloromethane was employed. The adhesive application and curing procedures adopted were the same as those detailed above.

RESULTS AND DISCUSSION

A. Synthesis and Characterisation of PPN resin

Scheme 1 shows the synthesis protocol for PPN. The precursor novolac was characterised by GPC. The system was devoid of free phenol, but contained oligomers with the degree of polymerisation of two and above. The peak molecular weight corresponded to 1600. Figure 1 shows the GPC traces of the precursor and the derived propargyl ether. The latter showed an increase in molecular weight on propargylation. The identical pattern distribution implies a uniform propargylation of the novolac. The propargyl ether derivative showed a peak molecular weight of 1980. The PPN resin was also characterised by FT-IR, which showed the characteristic strong absorption due to the ≡C-H bond of propargyl groups at 3272 cm⁻¹. The absorption due to C≡C appeared as a weak band at 2225 cm⁻¹. The FT-IR is shown in Figure 2. The extent of propargylation deduced from the hydroxyl value is 69%. The resin was a tacky, low melting solid.

B. Epoxy Curing and Cure Studies

Figure 3 shows the DSC of the PPN-EPN blend in presence of 1% TPP. The peak centred at 135°C is attributed to the phenol-epoxy cure and that at 235°C to the propargyl groups. The non-isothermal DMA shown in Figure 4 confirms the two-stage cure, where the curing is practically complete at 270°C. The isothermal DMA in Figure 5 confirms that the cure was completed in 120 min at 220°C. FT-IR substantiated the cure completion from the disappearance of the ≡C-H absorption at 3272 cm⁻¹ in the cured polymer (the spectrum of the cured polymer is included in Figure 2). The epoxy absorption at 930 cm⁻¹ also vanished in the spectrum of the cured system. Propargyl ether is known to undergo curing through the Claisen rearrangement and thermal polymerisation of the resultant chromene groups. Based on this, the dual cure of the blend is depicted in Scheme 1.

C. Adhesive Properties

Phenolics per se are poor adhesives for metal substrates. Reports on the adhesive properties of
propargyl ether resins are very few. Phenolic-epoxy systems are good adhesives. Hence, it was of interest to investigate the adhesive characteristics of the PPN-epoxy blend. The variation of LSS with phenol-epoxy ratio is shown in Figure 6 for EPN and in Figure 7 for DGEBA. The graphs also show the percentage retention of LSS at 100°C.

Scheme 1 Synthesis of PPN resin and curing with epoxy resin
The adhesive properties of the PPN resin were significantly enhanced by the reaction with epoxy. The optimum adhesive strength was observed with a phenol-epoxy equivalent ratio of 2:1 in both cases. Maximum high temperature retention was also shown for this composition. A small proportion of epoxy boosted the adhesion significantly. The strength was higher for DGEBA due to its better flexibility and...
lower crosslink density in this case, in contrast to the rigid EPN system. However, the high temperature retention was nearly identical for both systems.

Incorporation of thermoplastics generally enhances the adhesive properties of brittle matrices comprised of phenolics and phenolic-epoxies. Figure 8 shows the LSS of the PNEX-6535 system with varying proportion of polycarbonate and polysulfone. In both
cases, the LSS decreased on addition of the thermoplastics. The decrease was greater in the case of the PC system. Earlier investigations have shown that precipitation of such thermoplastics in the matrix is conducive to enhancing adhesion while its fine dispersion is detrimental for it\textsuperscript{16}. It may therefore be concluded that in PPN-epoxy matrix, both the thermoplastics are finely dispersed.  

Figure 5 Isothermal DMA of the PPN-EPN blend in presence of 1\% TPP at 220\textdegree{}C by parallel plate rheometry under controlled strain (0.01). Heating rate 10\textdegree{}C/min. Frequency, 2Hz

Figure 6 Variation of LSS and LSS retention at 100\textdegree{}C with phenol-epoxy ratio for PPN/EPN system
Figure 7 Variation of LSS and LSS retention at 100°C with phenol-epoxy ratio for PPN/DGEBA system

![Figure 7](image)

Figure 8 Dependency of LSS of PNEX-6535 on polycarbonate (PC) and polysulfone (PS) concentrations

![Figure 8](image)

Table 1 Properties of glass laminate PPN-EPN system

<table>
<thead>
<tr>
<th>Polymer Ref.</th>
<th>OH/EPOXY Equivalent Ratio</th>
<th>ILSS (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Compressive Strength (MPa)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNEX-100</td>
<td>100:0 (PPN)</td>
<td>30</td>
<td>390</td>
<td>165</td>
<td>&gt;350</td>
</tr>
<tr>
<td>PNEX-8515</td>
<td>85:15</td>
<td>28</td>
<td>320</td>
<td>140</td>
<td>&gt;350</td>
</tr>
<tr>
<td>PNEX-6535</td>
<td>65:35</td>
<td>30</td>
<td>375</td>
<td>140</td>
<td>300</td>
</tr>
<tr>
<td>PNEX-5050</td>
<td>50:50</td>
<td>25</td>
<td>340</td>
<td>174</td>
<td>270</td>
</tr>
</tbody>
</table>
D. Evaluation as Matrix in Glass Laminates

The PPN-EPN blends were evaluated as matrices in glass laminates. The data (averages of four measurements) given in Table 1 show that the composite properties were quite independent of the composition. The properties were good for the PPN resin and the presence of epoxy was not very helpful in strengthening the composite further. The dynamic mechanical analysis indicated that epoxy crosslinking led to a decrease in Tg. Whereas pure PPN gives Tg>300°C, the presence of epoxy brings it down to 270°C. The Tanδ curves for the four compositions are shown in Figure 9, and the Tg deduced from the Tanδ maximum is included in Table 1.

E. Thermal Stability

The TGA traces of the PPN-EPN system shown in Figure 10 imply that the addition of EPN decreases the thermal stability. Unlike a resole, the PPN resin starts losing weight only at around 400°C and is therefore comparatively stable. Addition of epoxy diminishes both the initial decomposition temperature (T_i) and the anaerobic char residue. The char residue at 750°C is inversely proportional to the epoxy-content. The dependence of T_i and the char residue on the epoxy-content depicted in Figure 11 confirms this. It can be concluded that the epoxy concentration has to be limited in order not to risk the thermal characteristics of the PPN-epoxy system.

CONCLUSIONS

Co-reaction of epoxy resin with a partially propargylated novolac resulted in a dual cure resin system with improved processibility. The resin system showed moderately good adhesion strength, which was optimised for a phenol/epoxy equivalent ratio of 2:1. Good retention of the properties was observed for the dual-cure system at 100°C. Replacing the novolac epoxy with the diglycidyl ether of bisphenol-A resulted in enhanced adhesion. Conventional matrix tougheners like polycarbonate and polysulfone were ineffective in improving the adhesion, possibly due to the fine dispersion of the additive in the matrix. Co-curing with epoxy led to easy processing without affecting the mechanical characteristics of the resultant glass composites. Minimising the epoxy-content is desirable to avoid sacrificing the thermal characteristics and Tg of the system.

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Figure 9 Tanδ curves for composites. (——) PNX-3050, (· · ··) PNX-6535, (· · ··) PNX-8515, (· · ··) PNX-100, Heating rate 10°C/min
Figure 10 TGA of PN-epoxy blend of varying composition in N2. (—) PNEX-100, (——) PNEX-8515, (……) PNEX-6535, (-----) PNEX-5050, Heating rate 10°C/min

Figure 11 Variation of initial decomposition temperature and char yield at 750°C for PPN/EPN system

REFERENCES