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Mechanical and Thermal Studies of Epoxy Resin Modified with Epoxidised Novolac from Phenol Naphthol Mixture

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Abstract

Diglycidyl ether of bisphenol A (DGEBA) resin can be modified by epoxidised novolac resins. The novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.8 in presence of oxalic acid catalyst. Novolac from phenol naphthol mixture synthesised and epoxidised using epichlorohydrin. Blends were prepared by mixing the epoxy resin with varying amounts of epoxidised phenol naphthol mixture and cured. The mechanical and thermal properties of the cured blends were determined and compared with those of the neat resin. In the presence of the epoxy hardener, the epoxy groups in both the matrix resin and naphthol resin are opened up resulting in chain extension and cross-linking. Napthol EPN shows improvement in water resistance and thermal properties without deteriorating the mechanical properties.

Keywords: Resin, Epoxy, Blending, Novolac,

1. Introduction

Epoxy resins constitute a class of thermosets containing more than one epoxide groups per molecule which are very reactive to many substrates (Collyer AA, 1994). DGEBA resin is prepared by reacting bisphenol A with epichlorohydrin (ECH) in the presence of caustic soda (Castan U.S. Patent,1948). DGEBA resins are widely used as a high performance thermosetting material in many industrial and engineering fields (Lee H., Neville K, 1967;Lubin G,1982, Jenish.P et al 2015) Un-modified epoxy resins based on bisphenol A-epichlorohydrin exhibit brittleness and low elongation after cure limited the application of these resins in many engineering fields (de Nograra FF et al 1996; Srinivasan, SA et al 1998) . So we have to modify the DGEBA resin. Novolacs can be prepared from phenol , and formaldehyde (Sandler SR and Karo W, 1992). The novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.8 in presence of oxalic acid catalyst. EPNs can be prepared by glycidylation of novolacs using epichlorohydrin (Cherian AB et al 2006).

In this study novolac resin was prepared from phenol (95 wt%) and naphthol (5 wt%) and epoxidised using epichlorohyrin . The synthesis was repeated with phenol and naphthol in varying molar compositions such as 90/10 and 20/80. These were designated by 5% naphthol EPN, 10% naphthol EPN and 20% naphthol EPN . These synthesized resins were used to modify the diglycidyl ether of bisphenol A resin and there mechanical and thermal properties were studied.

2. Experimental

2.1 Materials

Commercial grade epoxy resin GY 250, and the room temperature amine hardener HY 951 (polyamine) were supplied by Petro Araldite Pvt. Ltd. in Chennai. Phenol, Naphthol ,formaldehyde, epichlorohydrin, bezene, NaOH, oxalic acid, sodium sulphate were supplied by Merck India Ltd.

2.2 Curing of neat resin

Epoxy resin was mixed with 10wt% hardener and stirred well to make the mixture homogeneous. The resin was degassed in vacuum, poured into Teflon moulds and allowed to cure for

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24 hrs at room temperature. Post curing was done at 100°C for 4 hours.

2.3 Epoxidised novolac from phenol and naphthol mixture.

Novolac resin was prepared from phenol (95 wt%) and naphthol (5 wt%) . 1 mole of the novolac resin (1:0.8) was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 16 hours while 3 moles of sodium hydroxide in the form of 30 % aqueous solution was added drop wise. The rate of addition was maintained such that the reaction mixture remains at a pH insufficient to colour phenolphthalein. The resulting organic layer was separated, dried with sodium sulphate and then fractionally distilled under vacuum. The synthesis was repeated with phenol and naphthol in varying molar compositions such as 90/10 and 20/80. These were designated by 5% naphthol EPN, 10% naphthol EPN and 20% naphthol EPN.

2.4 Modification of epoxy resin with Epoxidised novolac from phenol and naphthol mixture

Epoxy resin was mixed with 5-20 wt% Epoxidised novolac from 95 % phenol and 5% naphthol mixture(5% Naphthol EPN) and stirred well. Then 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 100°C for four hours. The same procedure is repeated with 10% Naphthol EPN and 20% Naphthol EPN.

2.5 Characterisation Methods

2.5.1 Thermal studies

Thermal stability of the neat and modified cured resin samples was assessed using thermo gravimetric analyser (TGA Q50, TA Instruments) over a temperature range from room temperature to 600°C at a heating rate of 10°C/min.

2.5.2 Mechanical properties

The samples, after post curing, were tested for tensile strength, modulus and impact strength, taking six trials in each case. The tensile properties were determined on a Schimadzu Autograph Universal Testing Machine (ASTM D 638-89) and Izod impact strength was measured on a Zwick impact tester as per ASTM D 256 specifications.

2.5.3 Water Absorption

Water absorption was tested as per ASTM D 570. For the water absorption test, the specimens were dried in an oven for a specified 24hr and 80°C and then placed in a desiccators to cool. Immediately upon cooling, the specimens are weighed. The material is then submerged in water at room temperature for 24 hours. Specimens are removed, patted dry with a lint free cloth, and weighed.

2.5.4 Morphological Studies.

Morphology of the blends studied using scanning electron (SEM) micrographs. The SEM observations reported in the present study were made on the fracture surface of the tensile specimens.

3. Result and Discussion

3.1 Tensile properties

The variation in tensile strength obtained by adding varying amounts of modifier into epoxy resin is shows in Fig 1. Tensile strength increases with increase in concentration. 5% Naphthol EPN sample is found to give improved tensile strength compared to others.

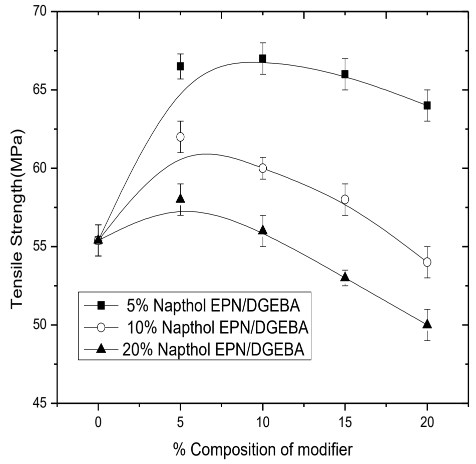

Fig.1 Tensile strength of Naphthol EPN modified resin Vs Naphthol EPN concentration

5% naphthol has relatively higher epoxy content and the cross-linking/chain extension reaction will be more effective in this cases. At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so tensile strength decreases.

Figure 2 gives the variation of elongation at break of the modified resin. There is only marginal improvement in elongation for DGEBA/5% naphthol EPN blends. This may be due to straightening of the entangled chains. At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so elongation decreases.

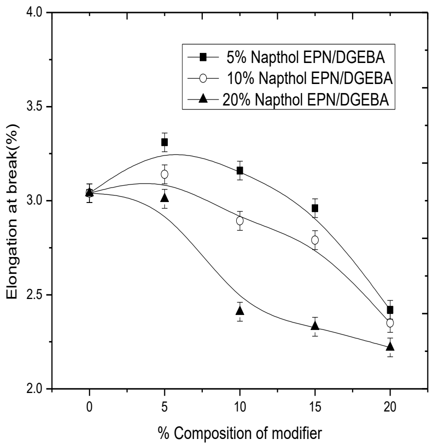

Fig.2 Elongation of Naphthol EPN modified resin Vs Naphthol EPN concentration

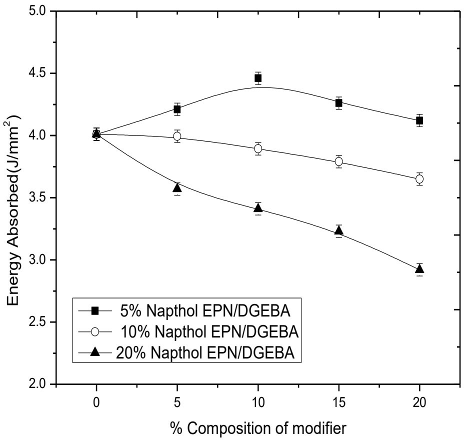

Fig.3 Elongation of Naphthol EPN modified resin Vs Naphthol EPN concentration

Figure 3 illustrates the effect of naphthol EPN on the energy absorbed by the blends at break. DGEBA/5% naphthol EPN blends absorb slightly more energy at break than the un-modified resin. This can be taken as a measure of slight improvement in the toughness of modified epoxy resins.

At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so energy absorption decreases.

The variation in impact strength of modified resin is given in Fig.4. Impact strength shows maximum values at about 5-10 weight % for the different samples. 5% naphthol EPN samples gave substantial improvement in impact strength due to better compatibility with the matrix resin.

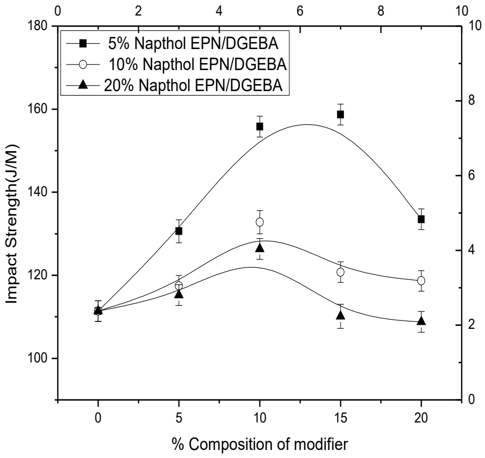

Fig.4 Elongation of Naphthol EPN modified resin Vs Naphthol EPN concentration

3.2 Water Absorption

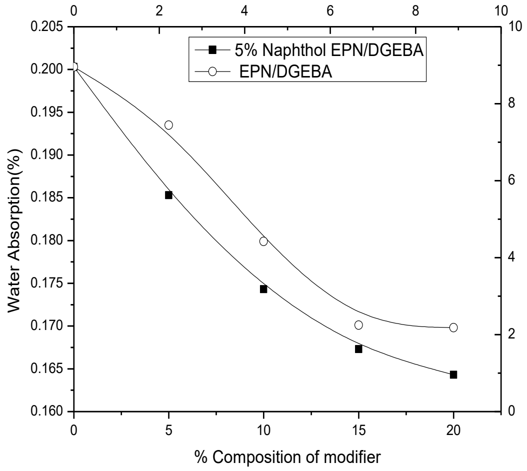

Fig. 5 Water absorption of modified resin Vs modifier Concentration

Modified sample shows better water resistance (Fig 5) may due to the presence of hydrophobic aromatic rings present in naphthol EPN. Naphthol EPN shows better water resistance than EPN.

3.3 Thermal properties

The TGA curves of the neat resin and DGEBA /5% naphthol EPN(10wt%) blend (Fig 6) show marginally better thermal stability for the modified sample An increased level of cross-linking

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as well as the presence of phenolic groups gives better thermal resistance to the blends. The Naphthol EPN modified sample gave 10.17 % residue at 600^0C compared to 6.7 % by the un-modified resin.

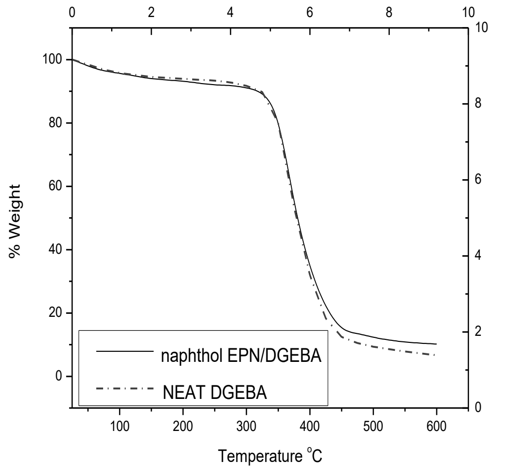
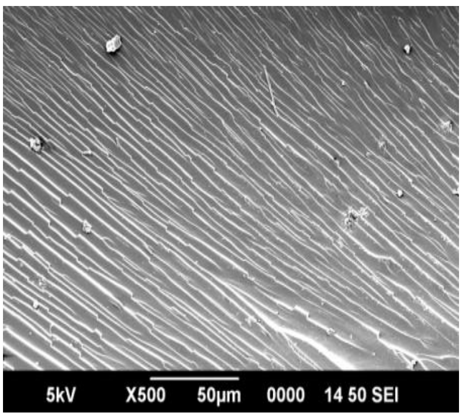


Fig.6 TGA curves for DGEBA and DGEBA/5% Naphthol EPN

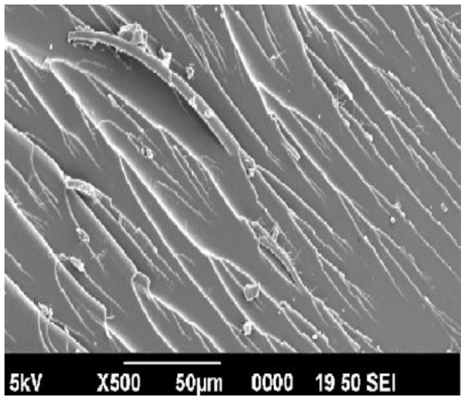
3.4. Morphological studies

Scanning electron micrographs of unmodified and 5% naphthol EPN modified epoxy resin fractured at low deformation are shown in Fig. 7. The micrograph (a) of the unmodified resin shows typical brittle fracture.

Naphthol EPN modified sample (b) shows multiple fracture paths. Stress whitening characteristic of crazing is also observed. All these features point to the improved toughness and load bearing characteristics of DGEBA/ Naphthol EPN blend.



(a)



(b)

Fig. 7 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/Naphthol EPN

4. Conclusions

Naphthol EPN can be synthesized from phenol naphthol mixture and can be used as a good modifier for DGEBA resin. 5% naphthol EPN blends absorb slightly more energy at break than the un-modified resin. This can be taken as a measure of slight improvement in the toughness of modified epoxy resins. At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so energy absorption decreases. Naphthol EPN shows improved thermal properties and water resistance due to the presence of naphthol group, without deteriorating the mechanical properties of the DGEBA resin. So Naphthol EPN can be used as a good modifier for DGEBA resin

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