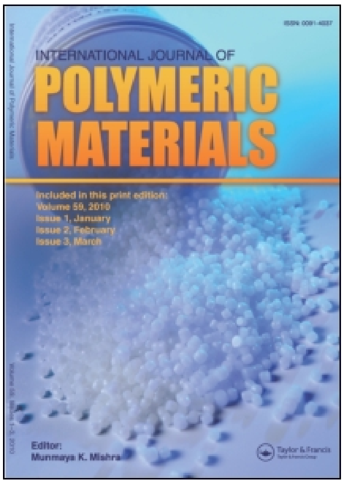

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Effect of Phenol/Formaldehyde Stoichiometry on the Modification of Epoxy Resin Using Epoxidized Novolacs

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Unmodified epoxy resins based on bisphenol A exhibit brittleness and low elongation after cure. This article reports the results of a study for improving the properties of epoxy resin by blending with suitable thermosets. Hybrid polymer networks of diglycidyl ether of bisphenol A (DGEBA) resin with epoxidized phenolic novolac resins (EPN) containing phenol and formaldehyde in different stoichiometric ratios were prepared by physical blending. The modified epoxy resins were found to exhibit improved mechanical and thermal properties compared to the neat resin. DGEBA resins containing 2.5 to 20 wt% of epoxidized novolac resins (EPN) prepared in various stoichiometric ratios (1:0.6, 1:0.7, 1:08, and 1:0.9) between phenol and formaldehyde were cured using a room temperature amine hardener. The cured samples were tested for mechanical properties such as tensile strength, modulus, elongation, and energy absorption at break. All the EPNs are seen to improve tensile strength, elongation, and energy absorption at break of the resin. The blend of DGEBA with 10 wt% of EPN-3 (1:0.8) exhibits maximum improvement in strength, elongation, and energy absorption. EPN loading above 10 wt% is found to lower these properties in a manner similar to the behavior of any filler material. The property profiles of epoxy–EPN blends imply a toughening action by epoxidized novolac resins and the extent of modification is found to depend on the molar ratio between phenol and formaldehyde in the novolac.

Keywords: epoxy resins, impact modification, phenolic epoxy novolacs, toughening

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INTRODUCTION

Epoxy resins are thermosetting polymers widely used for polymer composites, adhesives, high-performance coatings, potting, encapsulation, and numerous other applications. They possess more than one epoxy group per molecule and the structure is reactive to many functional groups leading to chain extension and/or crosslinking [1]. Unmodified epoxy resin based on bis-phenol A-epichlorohydrin reaction is found to exhibit brittleness and low elongation after cure.

One approach to improve epoxy resin toughness includes the addition of rubber particles as second phase [2]. Rubber particles acting as stress concentrators enhance shear localization [3]. A number of studies have been undertaken in recent years to investigate the mechanism of rubber toughening and to identify the right method of incorporating rubbers [4–6].

Incorporation of a rigid phase such as silica, kaolin, glass beads, and $CaCO_3$ fillers is another possibility. Fracture energy of brittle polymers can be significantly improved with the incorporation of particulate matter [7]. It has been reported that particulates increase the fracture energy of epoxy matrix at a specific volume fraction of the added particles and at the same time decrease the elongation and impact resistance [8–9]. The degree of toughness improvement was found to depend on both the volume fraction as well as particle size and shape of the filler [10]. Another work illustrates the use of hybrid modifiers—a combination of rubber particles and fillers—in toughening epoxy resins [11]. The addition of thermoplastics fillers is a more recent development [12]. Polyphenyleneether (PPE) [13] and polyphenyleneoxide (PPO) [14], polyetheresters [15], polyethersulphone [16], polyetheretherketones, and polyetherimides [17] have been employed for this purpose. Amine and hydroxy-terminated polysulphones have also been used as epoxy modifiers [18].

Chemical modification using other thermosets or reactive polymers has attracted increasing attention in recent years. A great deal of literature has been devoted to the toughening of epoxies using polyurethane as second phase to form interpenetrating networks [19]. Toughening of epoxy resin using polyurethane prepolymer as modifier via IPN grafting [20] and modification of epoxies by isocyanate-terminated polybutadienes [21] have been reported. Epoxy modification using aromatic polyesters [22], polycarbonate-polyurethanes [23], telechelic methacrylates [24], and chain-extended ureas [25] have been cited in the literature. The toughening effect of polyols on the epoxy matrix has been investigated using hydroxyl-terminated polyester resins as modifiers [26]. Silicon graft co-polymers [27], plastisol based on PVC, and diethylhexyl phthalate [28] have also been employed. Another approach is the incorporation of well known thermoset resins [29–30]. The mechanical properties of epoxy-unsaturated polyester interpenetrating networks indicate enhanced toughness of the modified matrix [31]. With compatible resinous modifiers, the epoxy may interact through active hydrogens to produce a variety of hetero polymers. In this study, bisphenol A epoxy resin is modified by blending with epoxidized novolacs. Although epoxidized novolacs are known to be brittle, hybrid polymer networks resulting from their blends are seen to have improved properties.

EXPERIMENTAL

Materials

Commercial grade diglycidyl ether of bisphenol A (DGEBA) epoxy resin 103 (wpe = 188) and hardener 301 (polyamine) (Atul Polymers India Ltd. Gujarat) were supplied by Sharon Engineering Enterprises, Cochin-22. Phenol, sodium hydroxide, oxalic acid, and epichlorohydrin were supplied by E. Merck India Ltd, Mumbai.

Preparation of Epoxidized Phenolic Novolacs

Novolac phenolic resins were prepared initially by reacting phenol and formaldehyde in various stoichiometric ratios, namely, 1:0.6, 1:0.7, 1:0.8, 1:0.9, respectively, in the presence of oxalic acid catalyst. The reaction mixture was refluxed on a water bath, while stirring continuously, for 2 h. When the resin separated from aqueous layer, the reaction was stopped. The resin was neutralized with sodium hydroxide, filtered, and vacuum dried.

The novolac resins obtained were epoxidized using a mol ratio of 1:5 between the resin and epichlorohydrin in presence of caustic soda. The reaction mixture was heated on a water bath for eight hours while three moles of sodium hydroxide in the form of 30% aqueous solution was added dropwise. The rate of addition of alkali was maintained such that the pH of the reaction mixture was sufficient to color phenolphthalein. The organic layer was separated, dried, and fractionally distilled under vacuum. The epoxidized novolacs are designated as EPN-1, EPN-2, EPN-3, and EPN-4, respectively. The epoxy equivalents (wpe) of the unmodified epoxy resin and the different epoxy novolac resins were determined by refluxing a known weight of the resin with concentrated HCl in pyridine medium and measuring the unreacted acid by back titration with standard alkali [32]. The epoxy equivalents (wpe) for these EPNs were found to be 181.8, 175, 169.5, and 202, respectively.

Modification of Epoxy Resin by Epoxy Novolacs

Initially, unmodified resin was cured at room temperature by using 10 wt% of the hardener. It was then degassed in vacuum and poured into a teflon tensile mold with dumb-bell–shaped cavities. Samples for water absorption and compression tests were cast separately in appropriate molds. Curing was done at room temperature for 24 h followed by post curing at 120°C for 4 h. Subsequently, blends were prepared by adding varying amounts of EPN (2.5 to 20 wt%) to the epoxy resin. The mixture was homogenized by gentle agitation using a stirrer and degassed in vacuum at 50°C. The blends were cast and cured by the procedure employed for the neat resin. Soxhlet extraction (in benzene) and swelling studies (in chloroform) [33] were carried out to determine the extent of crosslinking in the cured samples.

Testing Methods

The post-cured samples were tested for tensile strength, elongation at break, modulus, energy absorption (to break), hardness, and water absorption taking six trials in each case. Tensile properties were tested on a Shimadzu Autograph Universal Testing Machine (ASTM-D-638-89). A Shore D Durometer was employed for surface hardness measurements (ASTM-D-2240-86). Water absorption was tested as per ASTM-D-570.

Samples of both modified and unmodified resins were subjected to morphological studies using a scanning electron microscope (SEM), Cambridge Instruments Stereoscan S 360. A TA Instruments TGA Q 50 was used to investigate thermal degradation of the samples. A TA Instruments DSC Q 100 equipped with RCS cooling system was used to study thermal transitions in the samples at 10°C/min. The damping properties were measured using a fixed frequency (1 Hz) dynamic analyzer model DMA-983 from Dupont, USA. A temperature ramp was run from room temperature to 200°C at 1°C/min to observe the thermomechanical behavior of both unmodified and modified samples.

RESULTS AND DISCUSSION

The compatibility of EPN with epoxy resin primarily arises from their almost similar polarities. The epoxy groups in both EPN and epoxy resin are opened up by the curing agent, which triggers the crosslinking process. The simultaneous crosslinking of DGEBA and EPN can take place via the following pathways: (i) The hardener can give rise to −NH groups on opening the epoxy rings of both DGEBA and EPN. These can further initiate opening up of additional epoxy rings leading to a crosslinked network; (ii) The secondary hydroxyl groups generated from DGEBA by opening of the epoxy ring by the hardener can condense with the secondary hydroxyl groups generated from the opening of the epoxy rings in EPN; (iii) The EPN may contain un-epoxidized phenolic hydroxyl groups that may initiate opening of epoxy rings in DGEBA and those in EPN. The identification of the exact crosslinking reactions has not been attempted because of these complexities resulting from the extremely reactive environment. It is possible that all the aforementioned reactions concomitantly take place to some extent in the crosslinking process.

Morphology

Figure 1 is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Figure 2 shows the fractured surface of an epoxy-10 wt%–EPN-3 blend. There are distinct signs of increased energy absorption in this case. Multilevel fracture paths with wavy crests indicate energy absorption on a large scale during failure.

Thermal Properties

Thermogravimetry

The TGA curves of the neat resin and DGEBA–EPN-3 (10 wt%) blend (Figure 3) show marginally better thermal stability for the

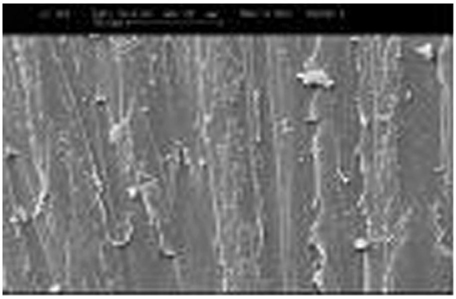


FIGURE 1 SEM micrograph of the fractured surface of unmodified DGEBA resin.

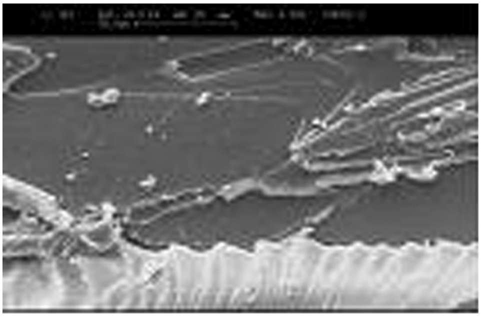


FIGURE 2 SEM micrograph of the fractured surface of EPN-3 (10 wt%) modified resin.

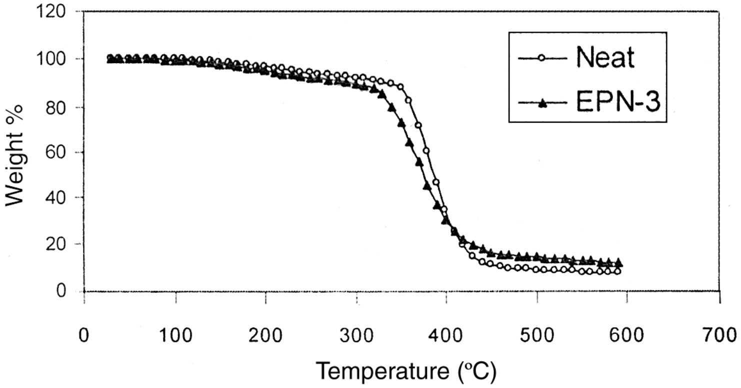


FIGURE 3 TGA curves for DGEBA and DGEBA–10% EPN-3 blend.

modified sample (Table 1). An increased level of crosslinking as well as the presence of phenolic groups gives better thermal resistance to the blends. The EPN-3 modified sample gave 11.39% residue at 600°C compared to 7.66% by the un-modified resin. The higher functionally

TABLE 1 Thermal Properties of DGEBA and DGEBA-EPN Blends

Sample	Onset temp. (°C)	Temp. of max. rate (°C)	Temp-half loss (°C)	Residue %
DGEBA (Neat)	310.56	386.12	367.24	7.664
DGEBA/EPN-3	312.34	374.22	375.11	11.39

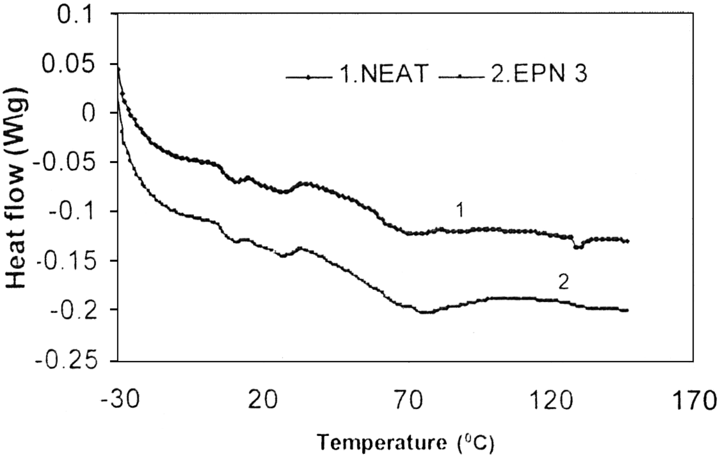


FIGURE 4 DSC thermograms of (1) DGEBA and (2) DGEBA–10% EPN-3 blend.

and phenolic content of novolac resins increase crosslink densities and improves thermal and chemical resistance.

Differential Scanning Calorimetry

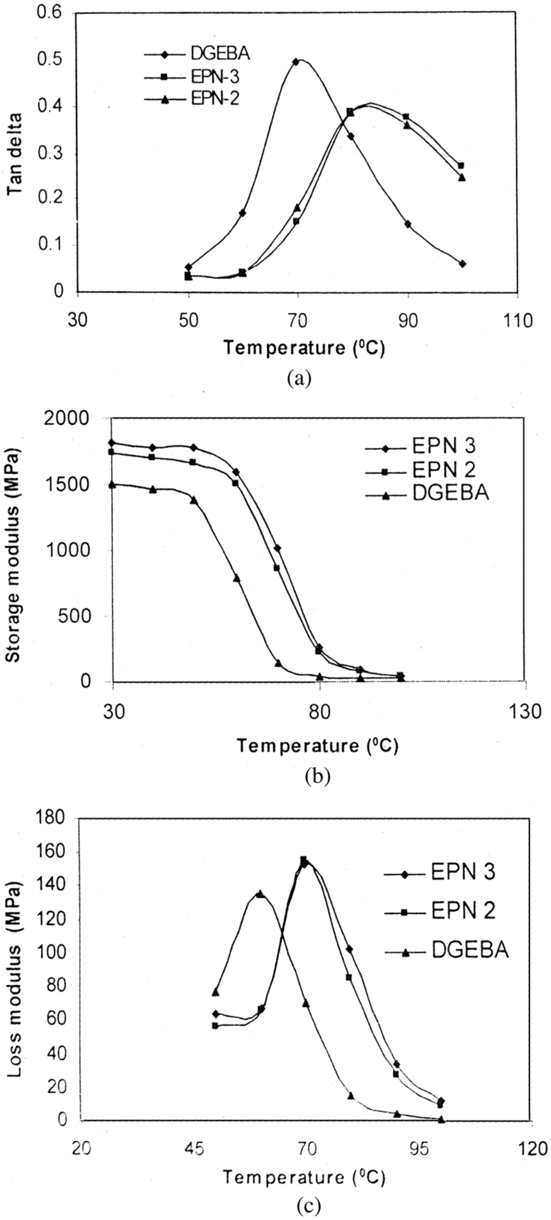
For the neat resin an endothermic transition is obtained at 70.64°C (T_g). The DSC thermograms reveal that addition of 10 wt% EPN-3 to the epoxy matrix shifts the T_g to higher temperature of about 78°C (Figure 4). This effect is in conformity with the higher level of crosslinking facilitated by EPN. This is in agreement with the data obtained from Soxhlet extraction and swelling studies (Table 2).

Dynamic Mechanical Thermal Analysis

The glass transition of neat epoxy obtained from DMA-tan δ curves (Figure 5a) (71.3°C corresponding to tan δ 0.497) is in agreement with the DSC measurement. Incorporation of EPN-3 (10 wt%) results in a broader transition that indicates better energy dissipation. Also, the

TABLE 2 Soxhlet Extraction and Swelling Data (DGEBA/EPN 10 wt%)

Samples	DGEBA	EPN-1	EPN-2	EPN-3	EPN-4
Soluble matter %	5.34	4.69	4.13	3.82	4.29
V_p	0.904	0.911	0.928	0.942	0.917



(a)

(b)

(c)

FIGURE 5 (a) DMA—Tan δ curves of DGEBA, DGEBA–10% EPN-3, and DGEBA–EPN-2 blends; (b) DMA—Storage modulus curves for DGEBA, DGEBA–10% EPN-3, and DGEBA–EPN-2; and (c) DMA–Loss modulus curves for DGEBA, DGEBA–10% EPN-3, and DGEBA–EPN-2.

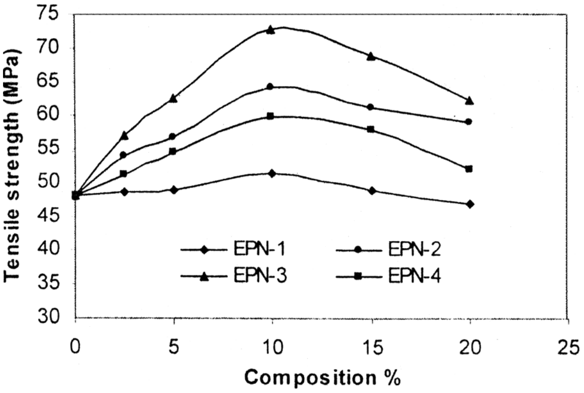


FIGURE 6 Tensile strength (MPa) of modified resin vs. EPN concentration (wt%).

decrease in height of tan δ with the addition of EPN points to a moderate plasticizing effect of epoxy novolacs. The damping peaks occur at lower tan δ values in the case of the blends due to sufficiently higher storage moduli. This is indicative of a greater extent of crosslinking in the blends [31]. The modified samples show a higher storage modulus (Figure 5b) than that of the neat resin thereby confirming this observation. The epoxy–EPN blends show higher loss modulus (Figure 5c) compared to the unmodified sample. A higher loss modulus causes more mechanical energy to turn into heat via molecular relaxation.

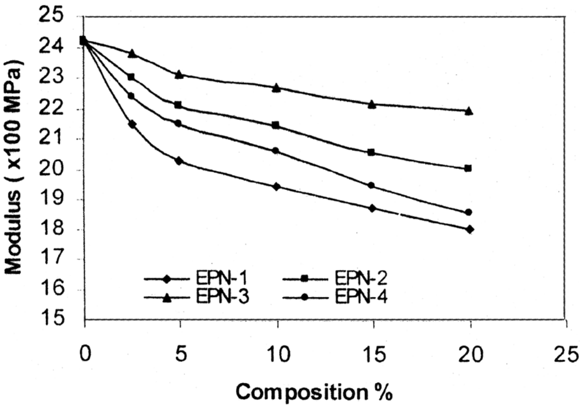


FIGURE 7 Modulus ($\times 10^2$ MPa) of modified resin vs. EPN concentration (wt%).

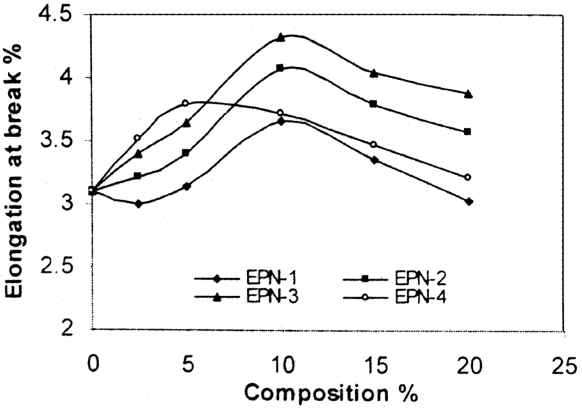


FIGURE 8 Elongation at break (%) of modified resin vs. EPN concentration (wt%).

Tensile Properties

Referring to Figure 6, tensile strength values obtained by blending epoxy resin with 2.5 to 20% epoxy novolacs are significantly higher than that of the unmodified resin. Tensile strength reaches a maximum at 10 wt% for EPN-3 beyond which the strength is found to decrease. The improvement in tensile strength over that of the base resin is due to a higher degree of crosslinking as well as chain

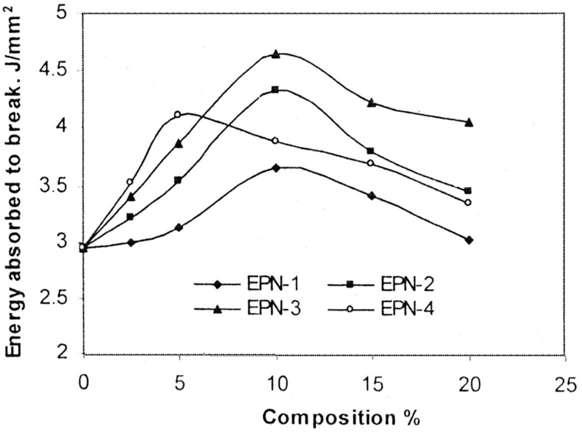


FIGURE 9 Energy absorbed (to break) by modified resin vs. EPN concentration (wt%).

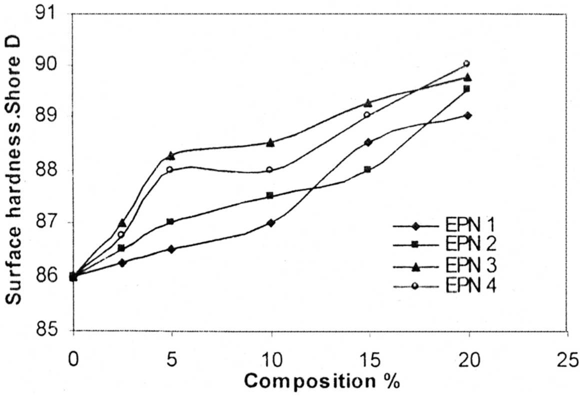


FIGURE 10 Surface hardness (Shore D) of modified resin vs. EPN concentration (wt%).

extension. This can also be attributed to some amount of entangling of the polymer chains. This results in increased tensile strength, lower extent of soluble matter, and increased volume fraction of polymer in the swollen samples, V_p. The modifying effect of EPN-3 is superior to that of the other EPNs due to its increased epoxy functionally, as evident from the wpe value.

Figure 7 shows the effect of epoxy novolacs on the tensile modulus. The slight reduction in modulus on addition of EPN shows improved

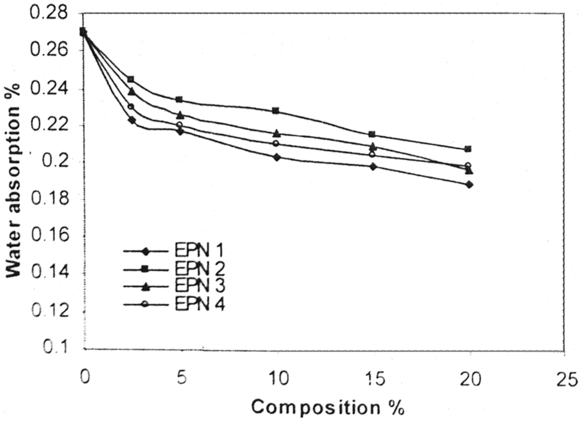


FIGURE 11 Water absorption (%) of modified resin vs. EPN concentration (wt%).

TABLE 3 Properties of Epoxy–EPN Blends (0–20%)

		% improvement/weight % EPN			
Property	DGEBA	EPN-1	EPN-2	EPN-3	EPN-4
Tensile strength (MPa)	48	7.32/10	53/10	70/10	24/10
Modulus (×100 MPa)	24.2	–25.6/20	–13/20	–10/20	–23/10
Elongation at break (%)	3.1	18.2/10	46/10	52/10	22.5/5
Energy absorbed (J/mm^2) (to break)	2.95	24/10	96/10	136/10	39/5
Surfaces hardness (Shore D)	86	3/20	4.2/20	4/20	4.7/20
Water absorption %	0.27	–31/20	–23/20	–27/20	–25/20

molecular flexibility. The effect on elongation at break is shown in Figure 8. Compared to unmodified resin the blends show an increase in elongation. Epoxy–EPN blends show maximum elongation at 10 wt% of epoxy novolac. In this case too EPN-3 enjoys clear superiority over the other epoxy novolacs used. A higher elongation may be the result of uncoiling of the entangled chains.

Figure 9 gives the variation of energy absorbed (to break) by the blends of epoxy resin with epoxy novolacs. This can be taken as a measure of toughness. At 10 wt% of EPN, the energy absorbed at break (about 135% of that of the neat resin) is maximum. The enhanced energy absorption may be attributed to a greater level of flexibility and capacity for spatial rearrangement.

Hardness and Water Absorption

Figure 10 indicates a general improvement in surface hardness upon blending epoxy resin with epoxy novolacs. However, the increase is only marginal. Water absorption of epoxy novolac–modified epoxy resins is given in Figure 11. The blends show increased water resistance. This is possibly due to a greater extent of methylene groups, which are not amenable to hydrogen bonding. The highest resistance is shown by epoxy–EPN-1 blend. This may be due to an excess of aromatic rings arising from the higher phenol content (1:0.6).

Table 3 summarizes the mechanical properties of epoxy–EPN blends. The maximum improvement acquired in each property and the corresponding concentration are tabulated.

CONCLUSION

This study revealed the effect of incorporating epoxidized phenolic resins of different phenol/formaldehyde molar ratios into an epoxy resin. In general, the blends show improved tensile strength and toughness. Of the epoxidized novolacs used, EPN-3 (P:F molar ratio = 1:08) gives the best results (70% improvement in tensile strength and 136% in energy absorption at break). There is a moderate overall improvement in thermal properties as well. Morphological studies point to improved energy absorption by the modified resin. A better insight into epoxy–EPN blends may be achieved only through investigations into the chemical reactions involved.

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