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Hybrid Polymer Networks of Epoxy Resin and Substituted Phenolic Novolacs

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Hybrid polymer networks of diglycidyl ether of bisphenol (DGEBA) resin and phenolic novolac resins were prepared and tested for mechanical properties, hardness, and water absorption. The novolacs employed were based on each of phenol and substituted phenols such as p-cresol, t-butyl phenol, and cardanol. Cardanol is the main constituent of cashew nut shell liquid (CNSL), a renewable resource. Blends containing 10–15 wt% of novolac resin show substantial improvement in properties. These properties show a declining trend with higher novolac loading. The stoichiometric ratio between phenol and formaldehyde in the novolacs was optimized (1:0.8) for maximum property enhancement. The property profiles of the epoxy/novolac networks show that novolacs are effective modifiers for commercial epoxy resin. Incorporation of novolacs of substituted phenols results in relatively greater improvement in energy absorption during failure.

Keywords: epoxy resin, modification, phenolic novolacs, toughening, cardanol

INTRODUCTION

Epoxy resins are thermosetting polymers widely used for polymer composites, adhesives, high-performance coatings, potting and encapsulation, and numerous other applications. They are known to possess more than one epoxy group per molecule and the structure is reactive to a variety of functional groups leading to chain extension and/or cross-linking. The type of epoxy group, its location within the

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molecule, and steric factors influence the reactivity of the resin [1]. Unmodified epoxy resin based on bis-phenol A and epichlorohydrin exhibits brittleness and low elongation after cure.

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

Incorporation of a rigid phase such as silica, kaolin, glass beads, and CaCO_3 fillers is another possibility. The fracture energy of brittle polymers can be significantly improved by the incorporation of particulate matter [7]. It has been reported that particulates increase the fracture energy of epoxy matrix 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]. Polyphenylene ether (PPE) [13] and polyphenyleneoxide (PPO) [14], poly etheresters [15], polyethersulphone [16], polyetheretherketones and polyetherimides [17] have been employed for this purpose. Silicon graft co-polymers [18], plastisol based on PVC, and diethylhexyl phthalate [19] also have been employed for modification.

Chemical modification using other thermosets or reactive polymers has attracted increasing attention in recent years. Amine and hydroxy-terminated polysulphones are examples [20]. A great deal of literature has been devoted to the toughening of epoxies using polyurethane as a second phase to form interpenetrating networks [21]. Toughening of epoxy resin using polyurethane prepolymer as modifier via IPN grafting [22] and modification of epoxies by isocyanate-terminated polybutadienes [23] have also been reported. Epoxy modification using aromatic polyesters [24], polycarbonate-polyurethanes [25], telechelic methacrylates [26], and chain-extended ureas [27] 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 [28]. Well-known thermoset resins [29–30] have also been used as modifiers. 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. Phenolic novolac-cured epoxy resins are

used for encapsulation due to their low water absorption and resistance to heat and electricity. They require an accelerator for completion of curing. Compared to standard bisphenol A resins, the high functionality of novolacs increases cross-link densities and improves thermal and chemical resistance. In this study, bisphenol A epoxy resin is modified by blending with different types of novolac resins. Although novolacs are brittle, the hybrid polymer networks consisting of epoxy and novolac resin blends are seen to have improved properties.

EXPERIMENTAL

Materials

Commercial grade DGEBA epoxy resin 103 and amine hardener 301 (Atul Polymers India Ltd, Gujarat) were supplied by Sharon Engineering Enterprises, Cochin-22. Phenol, p-cresol, t-butyl phenol, formaldehyde, sodium hydroxide, and oxalic acid were supplied by E. Merck India Ltd. (Mumbai). Cardanol was recovered from CNSL by distillation. The epoxy equivalent (wpe) of the epoxy resin was determined (ASTM-D1652-73) as 188 by the pyridinium chloride method [32].

Preparation of Phenolic Novolac Resin

Phenol novolac resin (PN) was prepared by reacting phenol and formaldehyde in molar ratio 1:0.8 in the presence of oxalic acid catalyst. The reaction mixture was refluxed in a water bath, while stirring continuously, for 2 h. When the resin separated from the aqueous layer, the reaction was stopped. The resin was neutralized with sodium hydroxide, filtered, and vacuum dried. Novolac resins from p-cresol, t-butyl phenol, and cardanol (designated as PCN, BPN, and CN, respectively) were also prepared by the same method.

Modification of DGEBA Resin

10 wt% of the prescribed hardener was added to the epoxy resin and homogenized. The mixture was degassed for a few minutes and then poured into appropriate teflon 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 novolac (2.5 to 20 wt%) to the epoxy resin. The blends were cast and cured by the procedure employed for the neat resin after adding the hardener. Soxhlet extraction using benzene and swelling studies in carbon tetrachloride [33] were carried out to determine the extent of cross-linking in the cured samples.

Testing

After post curing, the samples were tested for tensile strength, elongation at break, modulus, energy absorbed to break, compressive strength, hardness, and water absorption, taking six trials in each case. Tensile properties were tested in 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. Compressive strength was tested as per ASTM-D-695.

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. 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 obtain the thermomechanical behavior of unmodified and modified samples.

RESULTS AND DISCUSSION

Bisphenol A resins can be blended with other resinous materials containing reactive groups. On curing, interaction occurs to give a cross-linked copolymer. The compatibility of phenolic resins with epoxy resin primarily arises from their almost similar polarities. At high temperatures, the phenolic hydroxyl groups react with the epoxy groups leading to chain extension. In the presence of amine catalyst, the reaction of acidic phenolic hydroxyl groups with the epoxide ring is facilitated even at room temperature. Moreover, hydroxyl groups can catalyze the curing action of DGEBA. This catalytic effect of -OH on the curing of epoxide by amine has been reported in the literature [34]. The net result is a cross-linked polymer that can be expected to show the thermal resistance of phenolics and an overall improvement in mechanical properties because of the hybrid network.

Morphology

Figure 1 is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths are mostly straight and constitute failure bands. The fractured surfaces of epoxy-novolac blends (Figure 2a and b) show distinct signs of increased energy

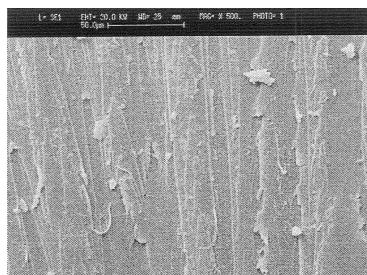


FIGURE 1 SEM micrograph of the fractured surface of unmodified DGEBA resin.

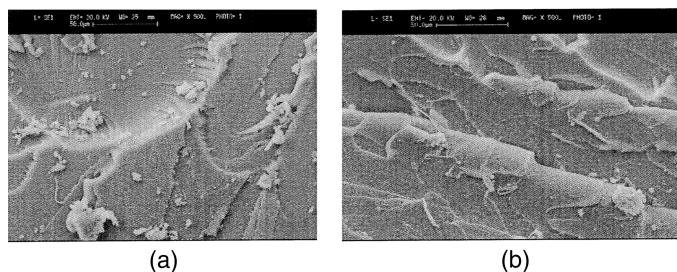


FIGURE 2 SEM micrographs of the fractured surfaces of PCN (15 wt%) and BPN (10 wt%) modified resins.

absorption. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure.

Soxhlet Extraction and Swelling Studies

The Soxhlet extraction and swelling data are given in Table 1. The cured modified samples yielded slightly smaller amounts of soluble matter compared to the unmodified sample. This is further confirmed

TABLE 1 Soxhlet Extraction and Swelling Data

Sample	DGEBA	PN 10%	PCN 10%	BPN 10%	CN 10%
Soluble matter %	5.34	4.88	4.581	4.692	5.083
V_p	0.904	0.914	0.928	0.921	0.901

by the slightly higher volume fraction of polymer in the swollen samples, V_p , values or the modified samples obtained from the swelling studies. This indicates cross-linking between epoxy resin and the modifier novolac resin.

Thermal Properties

The TGA curves of the neat resin and DGEBA/PCN (15 wt%) and DGEBA/CN (5 wt%) blends (Figure 3) show marginally better thermal stability for the modified samples. An increased level of cross-linking as well as the presence of phenolic groups gives better thermal resistance to the blends (Table 2). The PCN modified sample gave 8.193% residue at 600°C compared to 7.66% by the un-modified resin. However, the CN modified sample yielded less residue (6.88%) indicating its decreased ablative property. This may be due to the presence of the long aliphatic side chain in the cardanol molecule.

The DSC thermograms of the neat resin and its blend with 15 wt% PCN are given in Figure 4. For the neat resin an endothermic secondary transition is obtained at 70.64°C (T_g). Addition of 15 wt% PCN to the epoxy matrix shifts the T_g to higher temperature of about 77.47°C (Figure 4). This effect is in conformity with the higher level of cross-linking facilitated by the novolac. This is in agreement with the data obtained from Soxhlet extraction and swelling studies. The higher

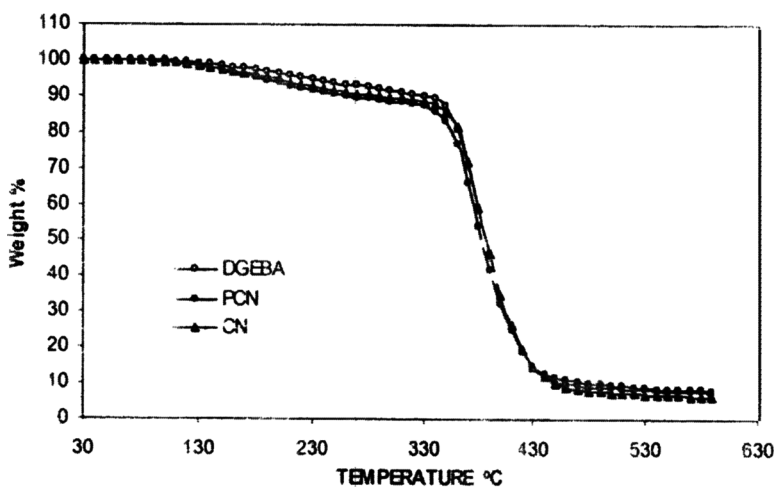


FIGURE 3 TGA curves for DGEBA and DGEBA/PCN (15 wt%) and DGEBA/CN (5 wt%).

TABLE 2 Thermal Properties of DGEBA and DGEBA/Novolac Blends

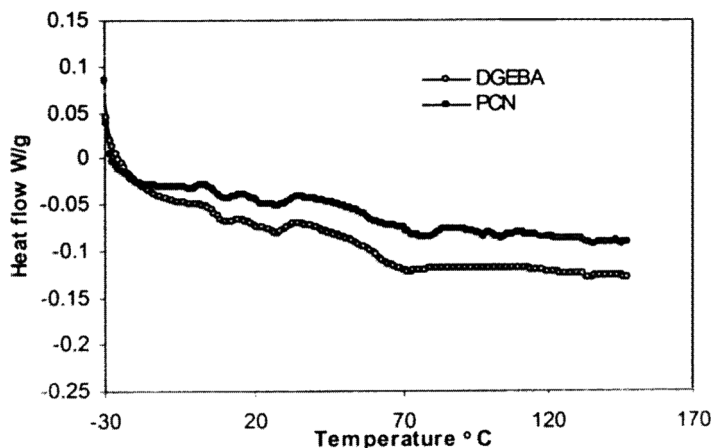
Sample	Onset temperature (°C)	Temperature maximum rate (°C)	Temperature half loss (°C)	Residue %
Neat resin	310.56	386.12	387.24	7.664
CN	315.98	379.86	386.63	6.883
PCN	308.50	376.72	383.03	8.193

functionality and phenolic content of novolac resins increase the cross-link densities and improves the thermal and chemical resistance.

The glass transition of neat epoxy obtained from DMA $\tan \delta$ curves (Figure 5a) (71.3°C corresponding to $\tan \delta = 0.497$) is in agreement with the DSC data. Incorporation of 15 wt% PCN ($\tan \delta = 0.4392$) and 10 wt% BPN ($\tan \delta = 0.4194$) shifts the T_g to higher values, 79.96°C and 79.53°C, respectively. The damping peaks occur at lower $\tan \delta$ values in the case of these blends due to higher storage moduli (Figure 5b). This is indicative of a greater extent of cross-linking in the blends [31]. The 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.

Tensile Properties

Referring to Figure 6, tensile strength values obtained by blending epoxy resin with 2.5 to 20% phenolic novolacs are significantly higher

**FIGURE 4** DSC thermograms of DGEBA and DGEBA/PCN (15 wt%) blend.

compared to that of the unmodified resin. Tensile strength reaches a maximum at 10–15 wt% of novolac 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 cross-linking as well as chain extension. This can also be attributed to some amount of entangling among the polymer chains. This results in increased tensile strength, lower extent of soluble matter, and increased V_p . The modifying effect of

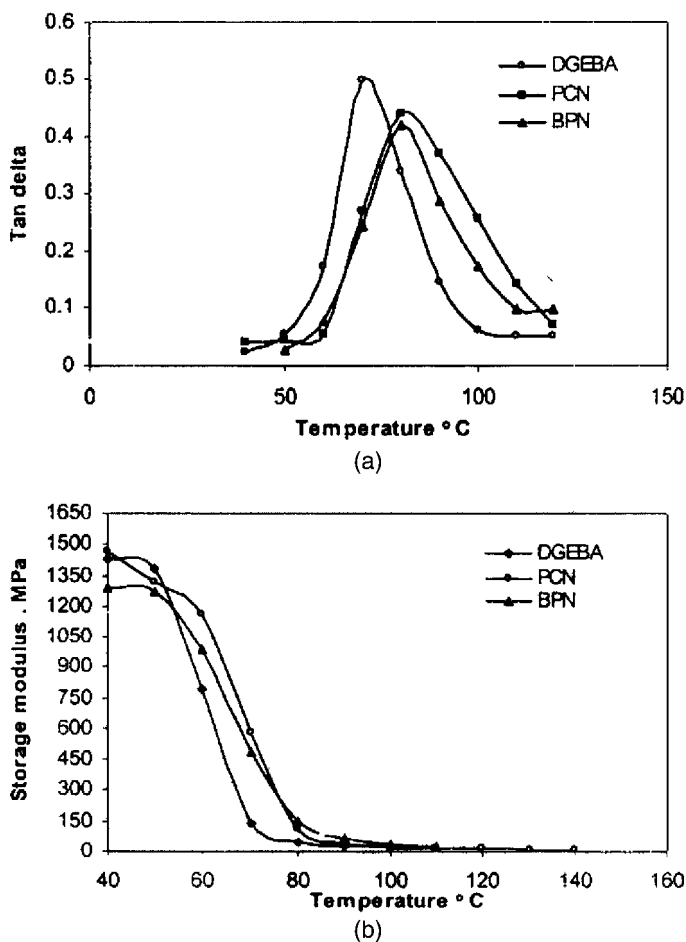


FIGURE 5 (a) DMA—Tan δ curves of DGEBA, DGEBA/PCN (15 wt%), and DGEBA/BPN (10 wt%); (b) DMA—Storage modulus curves of DGEBA, DGEBA/PCN (15 wt%), and DGEBA/BPN (10 wt%); (c) DMA—Loss modulus curves of DGEBA, DGEBA/PCN (15 wt%), and DGEBA/BPN (10 wt%).

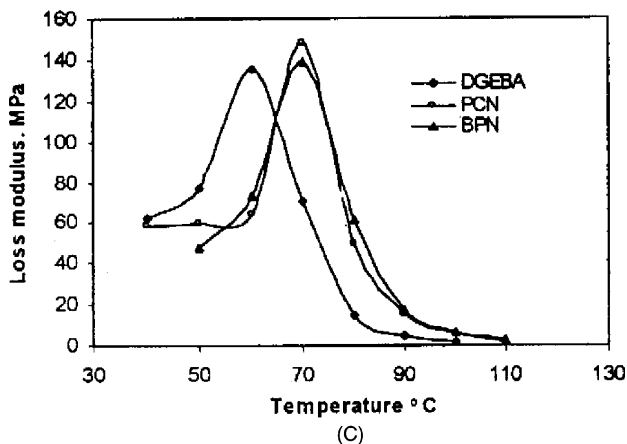


FIGURE 5 Continued.

PCN and BPN is found to be superior to that of the other novolacs. This can be due to a more linear structure resulting from the structures of p-cresol and t-butyl phenol, which have only two possible sites per molecule for condensation with formaldehyde.

Figure 7 shows the effect of epoxy novolacs on the tensile modulus. The slight reduction in modulus on addition of novolacs shows improved molecular flexibility. The effect on elongation at break is

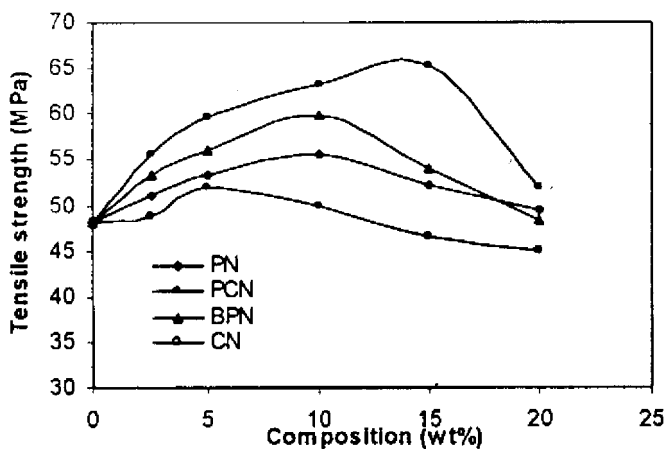


FIGURE 6 Tensile strength (MPa) of modified resin Vs novolac concentration (wt%).

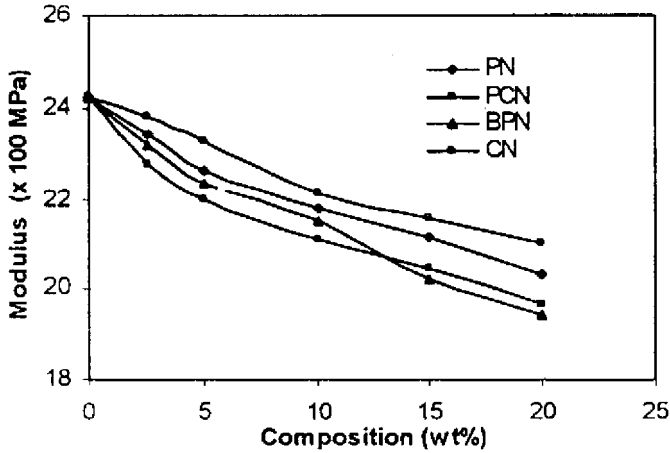


FIGURE 7 Modulus ($\times 10^2$ MPa) of modified resin Vs novolac concentration (wt%).

shown in Figure 8. Compared to unmodified resin the blends show an increase in elongation, Epoxy/PCN and epoxy/BPN blends show maximum elongation at 15 and 10 wt% of novolac, respectively, whereas the epoxy/CN blend shows maximum improvement in elongation at a lower novolac loading. A higher elongation may be the result of straightening of the entangled chains.

Figure 9 gives the variation of energy absorbed (to break) by the blends of epoxy resin with novolacs. This can be taken as a measure

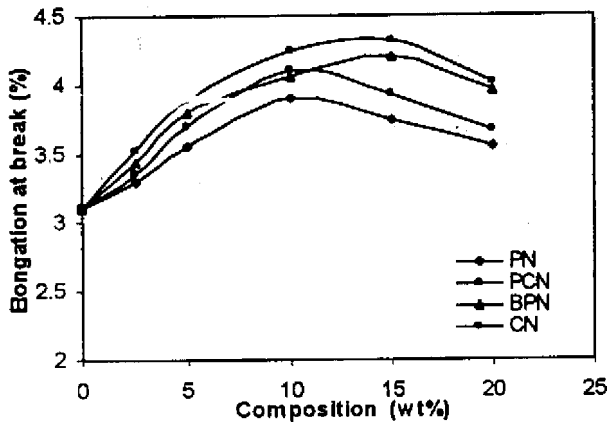


FIGURE 8 Elongation at break (%) of modified resin Vs novolac concentration (wt%).

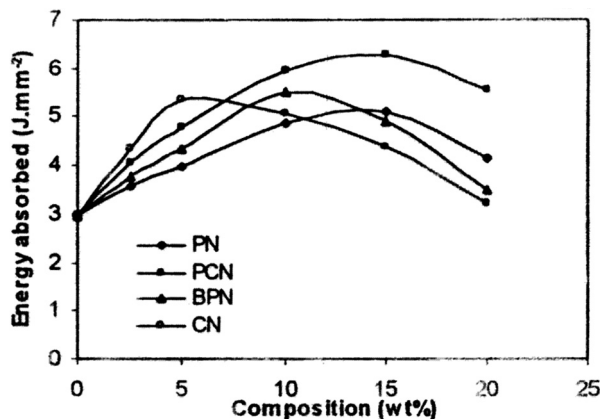


FIGURE 9 Energy absorbed (to break) (Jmm^{-2}) by modified resin Vs novolac concentration (wt%).

of the toughness. At 15 wt% of PCN, the energy absorbed at break (about 112% of that of the neat resin) is maximum. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement. The greater energy absorption shown by blends of para substituted phenol novolacs (novolacs of p-cresol and t-butyl phenol) confirms this observation. The variation in compressive strength for the blends is given in Figure 10. There is considerable increase in compressive strength for these blends

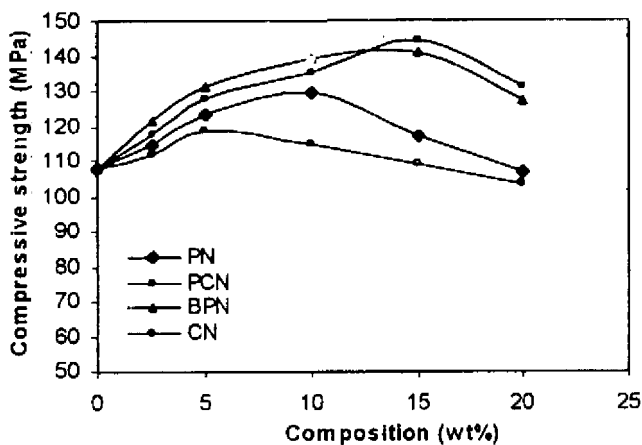


FIGURE 10 Compressive strength (MPa) of modified resin Vs novolac concentration (wt%).

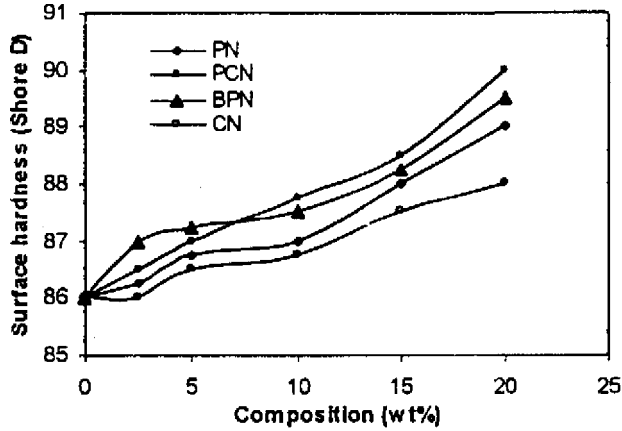


FIGURE 11 Surface hardness (Shore D) of modified resin Vs novolac concentration (wt%).

compared to the unmodified resin. This can also be explained in terms of increased levels of cross-linking. Blends with PCN and BPN show maximum compressive strength at 15 wt%.

Hardness and Water Absorption

Figure 11 indicates a general improvement in surface hardness upon blending epoxy resin with novolacs. However, the increase is only

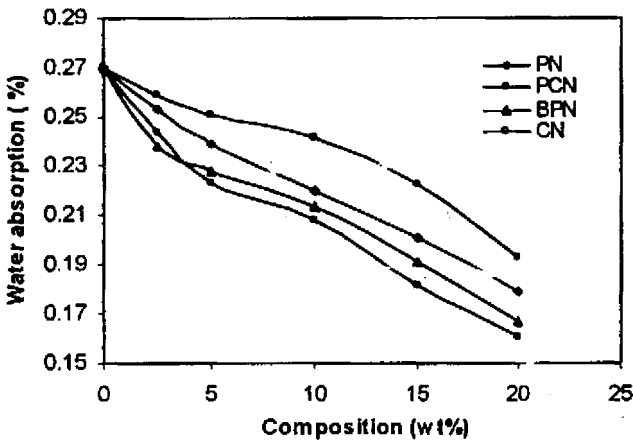


FIGURE 12 Water absorption (%) of modified resin Vs novolac concentration (wt%).

TABLE 3 Summary of Properties Epoxy/Phenolic Novolac Blends

Property	DGEBA	% Maximum improvement/composition (wt%)			
		PN	PCN	BPN	CN
Tensile strength (MPa)	48	18/10	38/15	26/10	9.5/10
Modulus ($\times 100$ MPa)	24.2	-16/20	-19.5/20	-20/20	-13/20
Elongation at break (%)	3.1	26/10	40/15	35.5/15	32/10
Energy absorbed (Jmm ⁻²)	2.95	72/15	112/15	89.7/10	81/5
Compressive strength (MPa)	108	20/10	35/15	31.5/10	11.25/5
Surface hardness (Shore D)	86	3.5/20	4.7/20	4.05/20	2.5/20
Water absorption (%)	0.27	-34/20	-42/20	-39/20	-29/20

marginal. Water absorption of novolac-modified epoxy resins is given in Figure 12. The blends show increased water resistance. This is possibly due to a greater extent of aromatic rings and methylene groups, which are hydrophobic in nature.

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

CONCLUSION

This study reveals the effect of individually incorporating different novolac resins into an epoxy resin by blending. In general, the blends show improved mechanical properties and toughness. Of the novolacs used, those prepared from para substituted phenols such as p-cresol (PCN) and t-butyl phenol (BPN) give the best results in modifying the energy absorption at break (112 and 91%, respectively). Interestingly, this has been achieved with simultaneous increase in tensile strength. Morphological studies also point to improved energy absorption by the modified resin. Epoxy/novolac blends also show considerable water resistance compared to the unmodified resin. Novolacs deserve consideration as effective modifiers for epoxy resin.

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