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The Modification of Commercial Epoxy Resin Using Cardanol - Formaldehyde Copolymers

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Unmodified epoxy resins based on bis-phenol A exhibit brittleness and low elongation after cure. Hybrid polymer networks of DGEBA resin and phenolic resol type resins were prepared from phenol (PF) and cardanol (CF), the main constituent of cashew nut shell liquid (CNSL), a renewable resource. The modified epoxy resins were found to exhibit improved elongation and energy absorption at break. Bisphenol A-epoxy resins containing 2.5 to 20 wt% of phenolic resols were prepared and tested for mechanical properties, water absorption, and so on. Blends containing 5 to 10 wt% of PF resin show substantial improvement in properties such as tensile strength, elongation, and energy at break, and these properties show a decline with higher resol loading. However, epoxy-CF blends show decreased tensile and compressive strengths. Resol resins made from cardanol-phenol mixtures (CPF) have improved energy absorption at break and this property increases with increase in CF content in the modifier resin. DGEBA/CPF blend containing cardanol and phenol in the mole ratio 3:2 is found to be superior in energy absorption at break. The property profiles of these blends imply a toughening action by resol type phenolic resins, especially cardanol-formaldehyde resins. The blends, however, show higher water absorption with only marginal improvement in certain other mechanical properties and surface hardness.

Keywords: epoxy resins, modification, impact modification, phenolic resins, resols

INTRODUCTION

Epoxy resins are thermosetting polymers widely used for polymer composites, adhesives high-performance coatings, potting, and

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encapsulation and numerous other applications. These resins have excellent mechanical and electrical properties, low cure shrinkage, good adhesion to most substrates, and resistance to moisture, thermal, and mechanical shock. Glycidyl ether epoxies such as diglycidyl ether of bis-phenol A (DGEBA) are the most commonly used epoxy resins.

Epoxy resins are cured by a variety of hardeners such as amines, acids, anhydrides, polyamides, and so on. Considerable effort has been focused on the impact modification of epoxy resins in recent years. Unmodified epoxy resin based on bis-phenol A-epichlorohydrin exhibits brittleness and low elongation after cure. This leads to low resistance to crack initiation and propagation. The high T_g values of epoxy thermosets are the result of crosslinked structures and this is achieved at the expense of toughness and damage tolerance.

There are several methods for impact modification of epoxy resins. Among these, modifications by a dispersed toughener phase and inorganic fillers [1–2] have been found to be the most effective.

The use of dispersed rubber particles as a second phase in the epoxy resin to increase the toughness of the brittle matrix has been extensively studied [3]. Rubber particles act as stress concentrators and enhance shear localization [4]. According to Pearson and Yee, smaller particles are more efficient in producing toughening effect [5]. The incorporation of liquid rubbers in epoxy resin has been investigated in detail and the reductions of T_g , modulus, and tensile strength have been observed as possible drawbacks in such modification [6–7]. A more recent work illustrates the benefits of hybrids (simultaneous use of filler and rubber) in toughening epoxies [8]. A great deal of literature has been devoted to the toughening of epoxies using polyurethane (PU) as second phase to form interpenetrating networks (IPNs) [9–11]. In this case the mechanical properties, especially tensile strength, are superior to those of unmodified epoxy polymers. Attempts to toughen epoxy resin using a PU pre-polymer as modifier by IPN grafting has been reported [12]. Modification of epoxies by isocyanate terminated polybutadienes [13], aromatic polyesters [14], polycarbonate-polyurethanes [15], telechelic methacrylates [16], and chain-extended ureas [17] 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 [18]. Silicon graft co-polymers [19], plastisol based on PVC, and diethylhexyl phthalate [20] and polyetherimides [21] also have been employed for modification of epoxy resins. Various types of thermoplastics have been used to modify epoxy resins [22–23]. Polyether sulphone [24], polyether ether ketones, and polyetherimides [25] have been employed for this purpose. Amine and hydroxy-terminated polysulphones are also used

as epoxy modifiers [26]. However, compared to rubber modification the extent of improvement achieved by thermoplastics is poor.

Another approach to the modification of epoxies is the incorporation of other thermoset resins [27–28]. The mechanical properties of epoxy-unsaturated polyester interpenetrating networks reveal enhanced toughness of the modified matrix [29]. Modification of epoxies by cresol novolac catalyzed by latent triphenyl phosphine has been reported [30]. The high functionality of novolacs increases the crosslink densities and improves the thermal and chemical resistance. When cured with phenolic hardeners epoxy resins give good adhesion, strength, chemical, and flame resistance. Phenolic novolac-cured epoxy resins are used for encapsulation due to their low water absorption and resistance to heat and electricity. Phenolic novolacs when used as curing agent in epoxies require an accelerator for the completion of curing.

Examples of low molecular weight butylated resols containing etherified and un-etherified methylol groups and phenolic hydroxyl groups being used as modifiers of epoxies are cited in the literature. This study has investigated blends of DGEBA with phenolic resol type resins and examined their properties, especially the energy absorbed to break. In particular, the influence of cardanol-based resins in the modification of epoxy resin is examined.

EXPERIMENTAL

Materials

Commercial grade bisphenol A epoxy resin 103 and hardener 301 (polyamide amine) were supplied by Atul Polymers India Ltd. through Ms. Sharon Engineering Enterprises, Kochi. Phenol, sodium hydroxide, oxalic acid, and formaldehyde were supplied by E. Merck India Ltd. Cardanol was recovered from CNSL by distillation. The epoxy equivalent (wpe) of the epoxy resin (188) was determined by refluxing a known weight of the resin with concentrated HCl in pyridine medium and measuring the un-reacted acid by back titration with standard alkali [31].

Preparation of PF Resol Type Resins

Phenolic resol resin (PF) was prepared using phenol (1 mol) and formaldehyde (1.5 mol) in the presence of caustic soda catalyst. The reaction mixture was refluxed in a water bath, while stirring continuously, for 2 h. After the reaction was over, the resin was neutralized with

oxalic acid solution till the resin became acidic to litmus. the resin layer was separated, dried, and then distilled in vaccum. Resol type resins derived from cardanol (CF) and cardanol-phenol mixtures were also prepared at different compositions such as 20/80, 40/60, 60/40 (designated as CPF 1:4, CPF 2:3, CPF 3:2, respectively) using the same method

Modification of DGEBA Resin by PF Resins

Unmodified epoxy resin was cured at room temperature by 10 wt% of the polyamide hardener. The resin was degassed and then poured into teflon molds with dumb-bell-shaped cavities coated with a release agent. 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, varying amounts of the PF resin containing 2.5 to 20 wt% of resol were added to the epoxy resin and mixed well by mechanical stirring. The resin mixture was degassed in vaccum at 60°C and cured by the procedure employed for the neat resin.

Testing Methods

The samples after post curing were tested for tensile strength, elongation at break, modulus, energy absorbed to break, compressive strength, hardness, and water absorption taking five 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 the thermal degradation of the samples. TA Instruments DSC Q 100 equipped with RCS cooling system was used to study thermal transitions in 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 thermo-mechanical behavior of unmodified and modified samples.

The cured samples were also subjected to Soxhlet extraction and swelling studies. For swelling studies, samples of approximately 10 mm diameter and 2 mm thickness were weighted and allowed to

swell in excess of carbon tetrachloride. The swollen samples were taken out of the solvent every 24 h, wiped dry, and weighed. When equilibrium was reached, the swollen samples were dried in vacuum and weighed. The volume fraction of the resin (V_p) in the swollen samples was calculated. V_p is linearly [32] related to the crosslink density of the polymer sample.

The samples for Soxhlet extraction were ground to particles of about 2 mm diameter and packets containing 2 g of the sample in Whatman No.1 paper were extracted with benzene in a Soxhlet apparatus for 48 h. The difference in weights of the packets gave the soluble matter, and the percentage of soluble matter was calculated.

RESULTS AND DISCUSSION

The compatibility of phenolic resins with epoxy resin primarily arises from their almost similar polarities. During blending of epoxy resin with PF resin the following reactions can take place: (i) When epoxy resin is blended with phenol-formaldehyde resin, the methylol group in the resol resin can condense with the secondary hydroxyl group of the epoxy system to form crosslinked structures; (ii) at high temperatures, the phenolic hydroxyl groups may react with the epoxy groups leading to chain extension; (iii) the resol resin can also react with the amino group of the hardener through the methylol groups giving $-\text{CH}_2-\text{NH}-$ groups, which in turn can open up epoxy rings. Moreover, hydroxyl groups can catalyze the curing action of DGEBA. This catalytic effect of $-\text{OH}$ on the curing of epoxide by amine has been reported in the literature [33–34]. The net result is a crosslinked polymer that exhibits chemical and heat resistance.

Morphology

Figure 1 is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture [35]. Fracture paths are mostly straight and constitute failure bands from bottom to top. The fracture surface is characterized by pinpoint crazes within the material. Figure 2 shows the fractured surface of an epoxy–PF blend. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure, and increased toughness.

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



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

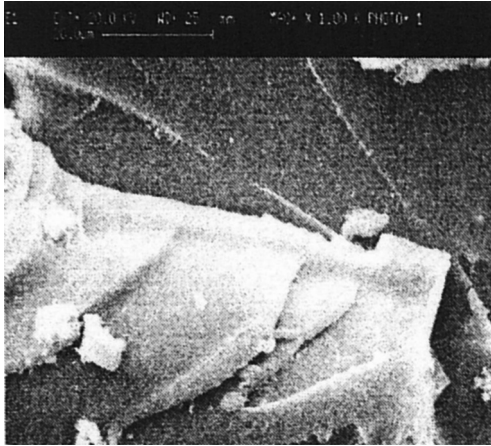


FIGURE 2 SEM micrograph of the fractured surface of PF (10 wt%) modified resin.

TABLE 1 Soxhlet Extraction and Swelling Data

Sample	DGEBA	5% PF	15% PF	5% PF	15% CF
Soluble matter %	5.34	5.21	5.312	5.282	5.36
V_p	0.904	0.910	0.917	0.907	0.897

matter compared to the unmodified sample. This is further confirmed by the slightly higher V_p values of the modified samples obtained from the swelling studies. This indicates crosslinking between epoxy resin and the modifier resin.

Thermal Properties

The TGA curves of the neat resin and DGEBA–10% CF blend are shown in Figure 3. The CF modified resin shows higher onset and half-loss temperatures than the unmodified sample as shown in Table 2. However, the CF modified sample yielded less residue (6.448%), indicating its decreased ablative property. This may be due to the presence of a long aliphatic side chain in the cardanol molecule.

The DSC thermograms of the neat resin and its blends with PF (10 wt%) and CF (10 wt%) are given in Figure 4. For the neat resin an endothermic secondary transition is obtained at 70.64°C (T_g). For the PF (10 wt%) and CF (10 wt%) blends a single T_g each is recorded indicating their homogeneous nature. Figure 5a–5c illustrate the DMA-tan δ , loss modulus and storage modulus curves, respectively. The glass transition of neat epoxy obtained from DMA-tan δ curves (71.3°C corresponding to tan $\delta = 0.497$) is in agreement with the DSC measurement. Incorporation of 10 wt% PF and 10 wt% CPF 3:2

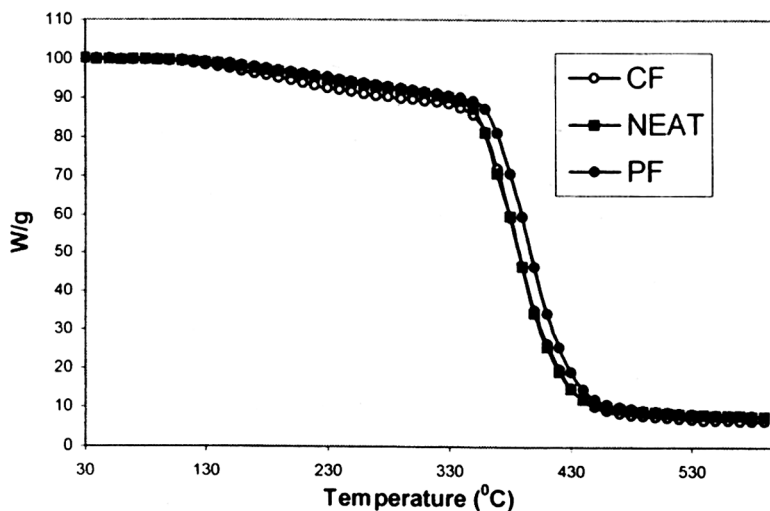
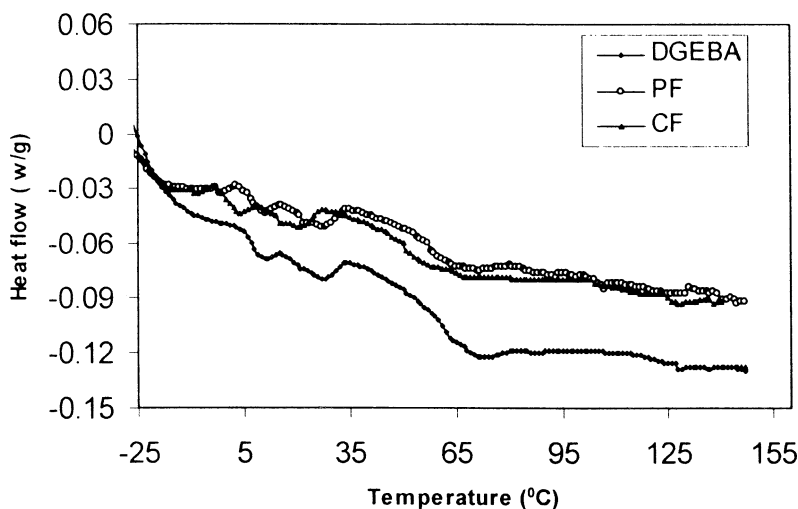


FIGURE 3 TGA curves for the DGEBA, DGEBA/10% PF, and DGEBA/10% CF blends.

TABLE 2 Thermal Properties of DGEBA and DGEBA-PF/CF Blends

Sample	Onset temperature (°C)	Temperature maximum rate (°C)	Temperature half loss (°C)	Residue %
Neat resin	310.56	386.12	367.24	7.664
CF blend	315.98	379.86	386.63	6.448
PF blend	317.43	381.22	377.67	7.721

**FIGURE 4** DSC thermograms of DGEBA, DGEBA/10% PF, and DGEBA/10% CF blends.

shifts the T_g to higher values, 79.53°C and 81.6°C, respectively. The damping peaks occur at lower $\tan \delta$ 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. In general, a higher crosslinked material would show higher storage modulus. The DGEBA–PF and DGEBA–CPF blends show higher storage moduli.

Mechanical Properties

Tensile Properties

Referring to Figure 6, tensile strength values obtained by blending epoxy resin with phenol-formaldehyde resin are higher compared to that of the unmodified resin. Tensile strength reaches a maximum

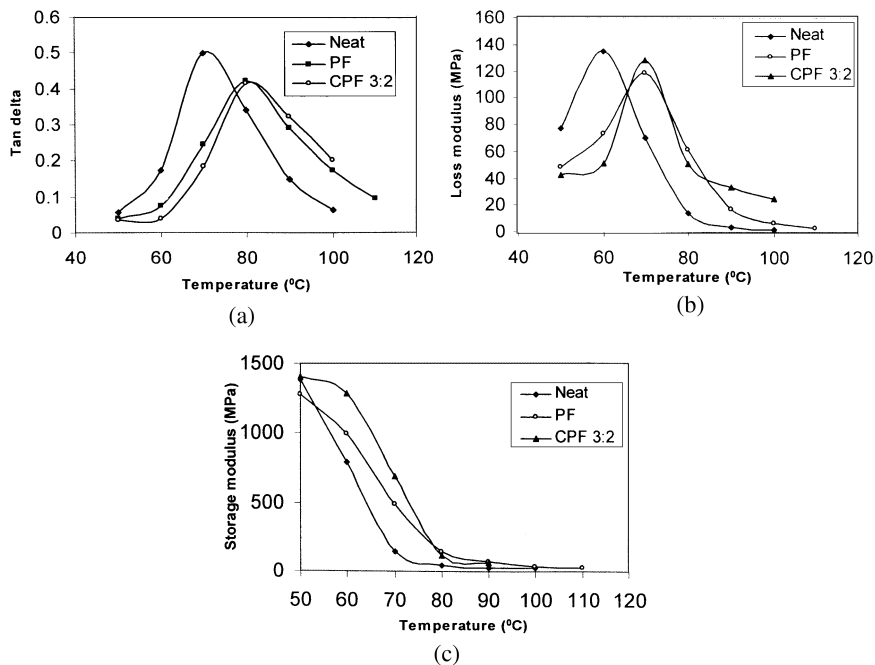


FIGURE 5 (a) DMA—Tan δ curves of DGEBA, DGEBA/10% PF, and DGEBA/10% CPF (3:2) blends; (b) DMA—Loss modulus curves of DGEBA, DGEBA/10% PF, and DGEBA/10% CPF (3:2); (c) DMA—Storage modulus curves for DGEBA, DGEBA/10% PF, and DGEBA/10% CPF (3:2).

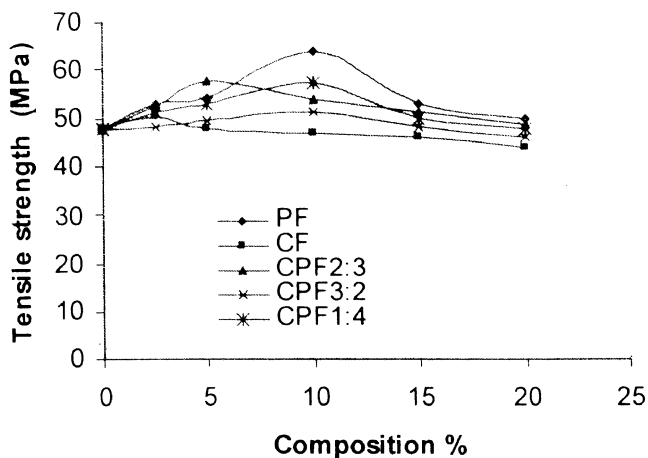


FIGURE 6 Tensile strength (MPa) of resol modified resin vs. phenolic resol concentration (wt%).

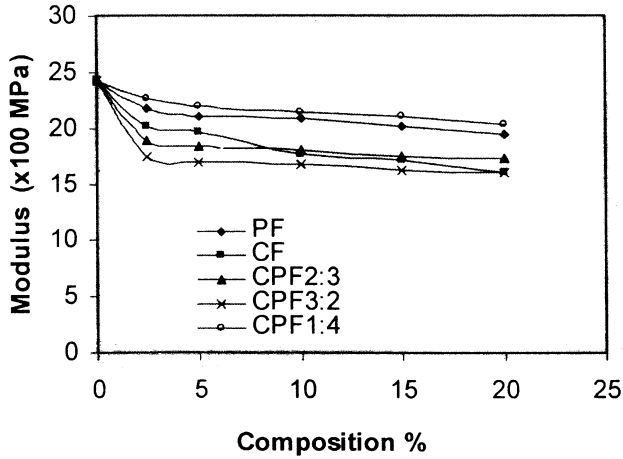


FIGURE 7 Modulus ($\times 10^2$ MPa) of modified resin vs. phenolic resin concentration (wt%).

on adding progressively larger amounts of PF, beyond which the strength is found to be lower. The improvement in tensile strength over that of the base resin at all percentages of the PF resin resins considered is due to the high degree of compatibility and enhanced cross-linking. At a certain composition of the blend the degree of crosslinking becomes optimum, beyond which further addition of resin

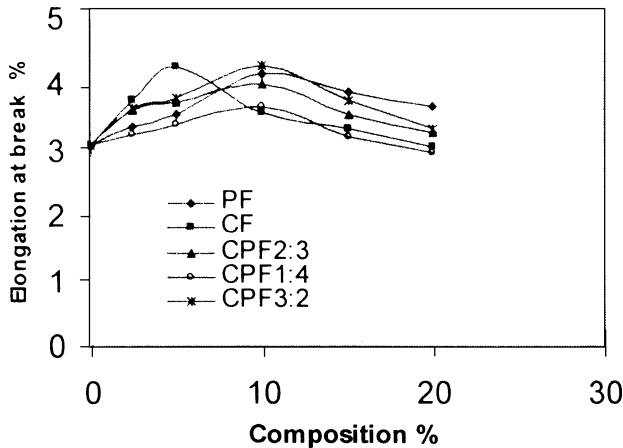


FIGURE 8 Elongation at break (%) of modified resin vs. phenolic resin concentration in (wt%).

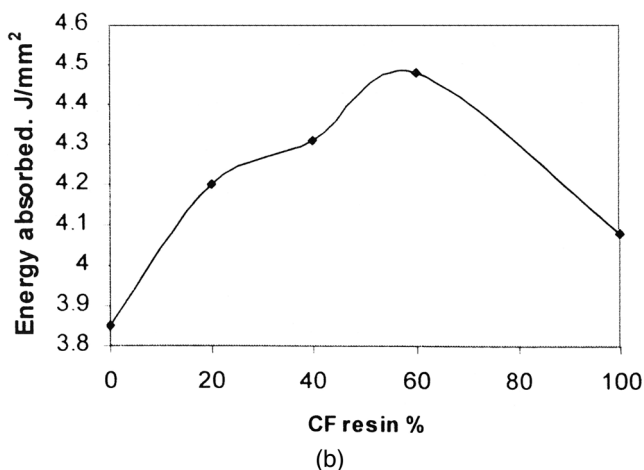
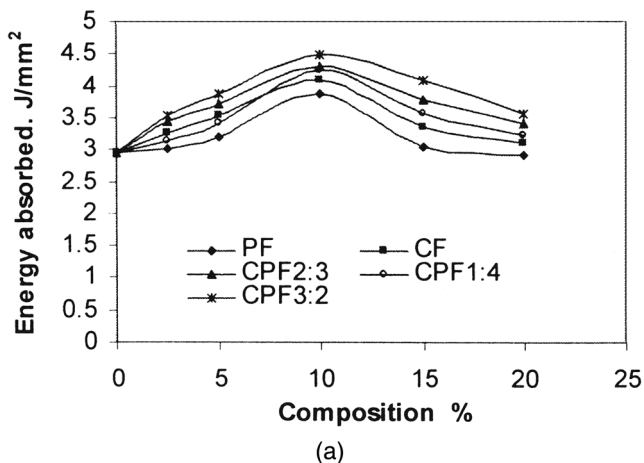


FIGURE 9 (a) Energy absorbed (to break) by modified resin vs. phenolic resol concentration (wt%); (b) Energy absorbed (to break) by modified resin vs. CF concentration in the modifier resin.

does not show any strengthening effect. Maximum strengthening occurs at about 10% resol concentration for most cases. However, incorporation of cardanol generally lowers the tensile strength. This can be attributed to the bulky nature of the cardanol molecule with a long aliphatic side chain, which can hinder crosslinking to some extent.

Figure 7 shows the effect of phenolic resol type resins on the tensile modulus. The change in modulus on addition of phenolic resins is only moderate. The modulus of epoxy-phenolic blends is lower than that for

the neat resin indicating flexibility of the polymer network. This effect is pronounced in the case of epoxy-CF blends, suggesting the ability of CF to reduce the inherent brittleness of the epoxy matrix.

The effect of addition of phenolic resols on elongation at break is given in Figure 8. Compared to unmodified resin, the blends show substantial improvement in elongation, especially at lower modifier concentrations. In particular, incorporation of CF induces enhanced flexibility of the epoxy matrix. This may be due to loose packing of the polymer chains by virtue of the peculiar branched structure of cardanol.

The extent of toughening attributed to the epoxy resin due to phenolic blending is measured in terms of the energy absorbed to break. Figure 9a gives the variation of energy absorbed by the blends of epoxy resin with phenolic resol resins. The blends absorb more energy than the neat resin. The enhanced energy absorption indicates inherent toughening produced in these blends, and this is probably due to enhanced flexibility of the polymer chains. The epoxy-CF blend exhibits better energy absorption than the epoxy-PF blend. This may be due to the bulky structure of cardanol molecule with a long side chain, which gives molecular flexibility. The epoxy-CPF mixtures show increased energy absorption compared to those with PF or CF alone. The energy absorbed to break increases with increase CF content in the resin mixture up to about 60% CF concentration, as given in Figure 9b. The variation in compressive strength for the blends of epoxy resin with various resols follows a trend similar to that of tensile strength (Figure 10). There is increase in compressive strength for

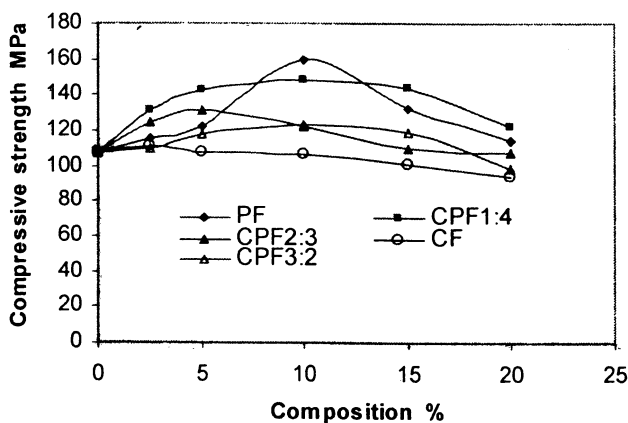


FIGURE 10 Compressive strength (MPa) of modified resin vs. phenolic resol concentration (wt%).

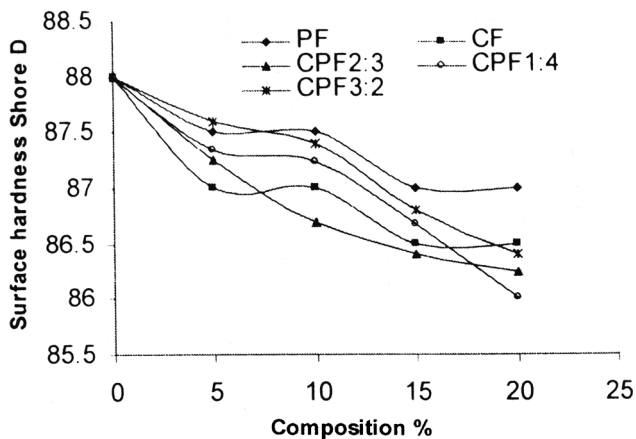


FIGURE 11 Surface hardness (ShoreD) of modified resin vs. phenolic resol concentration (wt%).

PF blends compared to the base resin. However, the epoxy-CF blends show only marginal improvement in compressive strength. The enhanced compressive strength may be due to the capacity for spatial molecular rearrangement.

Surface Hardness

Figure 11 indicates the variation in surface hardness upon blending epoxy resin with phenolic resols. The epoxy/resol blends generally

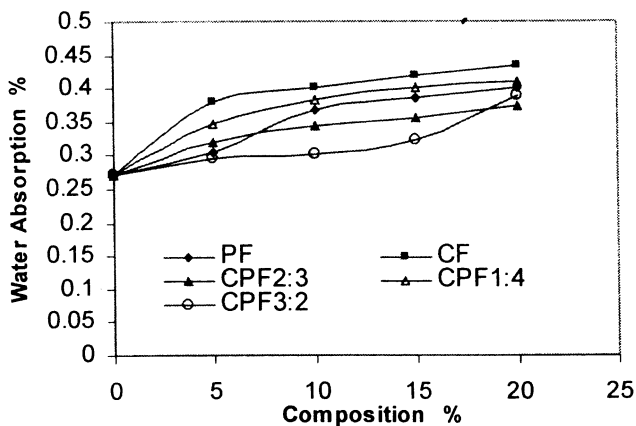


FIGURE 12 Water absorption (%) of modified resin vs. phenolic resol concentration (wt%).

TABLE 3 Summary of Properties of Epoxy-Phenolic Resol Blends

Properties	% Improvement/Composition (wt%)					
	Neat	PF	CF	CPF 2:3	CPF 1:4	CPF 3:2
Tensile strength (MPa)	48	40.2/10	5/2.5	20/5	19/10	7/10
Modulus ($\times 10^2$ MPa)	24.2	-19.4/20	-34/20	-27.7/20	-16/20	-34/20
Elongation at break (%)	3.1	34.5/10	38.8/5	29/10	20/10	38.5/10
Energy absorbed (J/mm ²)	2.98	46/10	53.7/10	71.4/10	62.3/10	82.7/10
Compressive strength (MPa)	108	47.2/10	3.2/2.5	21.3/5	37/10	14/10
Hardness Shore D	86	3.48/20	4.65/20	2.32/20	4.06/20	3.6/20
Water absorption (%)	0.27	48/20	57/20	43/20	52/20	62/20

show a slight decrease in surface hardness compared to the unmodified resin although in a few compositions there is hardly any decrease.

Water Absorption

Water absorption of various phenolic resol-modified epoxy resins is given in Figure 12. Epoxy-PF blends are found to be inferior in water resistance to the unmodified epoxy resin. Especially at higher resol concentrations water absorption is found to be high. This can be due to the presence of methylol functionalities capable of hydrogen bonding with water.

Table 3 summarizes the effect of adding varying amounts of phenolic resol resins in the base resin. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

CONCLUSION

The study reveals the effect of incorporating cardanol- and phenol-based resol type resins in epoxy resin by physical blending. Among the various resol resins used for blending those from phenol-cardanol mixtures are found to be superior in energy absorption to PF or CF resins used alone. Properties such as energy absorption and elongation at break reach a maximum at 60% cardanol content in a cardanol-phenol modifier resin. Interestingly, the increase in energy absorption (to break) has been achieved with simultaneous increase in tensile strength for the phenolic resins. Even though cardanol-based resins show improvement in mechanical properties, they are slightly inferior in thermal and ablative properties. A better insight to epoxy-resol blends can be achieved only through investigations into the complex chemical reactions involved during the curing of the blends. The use of cardanol in the formulation is attractive in view of its low price and renewable nature.

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