

Epoxidized Phenolic Novolac: A Novel Modifier for Unsaturated Polyester Resin

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Received 9 September 2004; accepted 15 June 2005

DOI 10.1002/app.23132

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Unsaturated polyester resins (UPRs) are used widely in the fiber-reinforced plastics (FRPs) industry. These resins have the disadvantages of brittleness and poor resistance to crack propagation. In this study, hybrid polymer networks (HPNs) based on UPR and epoxidized phenolic novolacs (EPNs) were prepared by reactive blending. A HPN is composed of a backbone polymer containing two types of reactive groups that can take part in crosslinking reactions via different mechanisms. EPNs were prepared by glycidylation of novolacs using epichlorohydrin. The novolacs had varying phenol: formaldehyde ratios. Blends of unsaturated polyester with EPN were then prepared. The physical properties of the cured blends were compared with those of the control resin. EPN shows good miscibility and

compatibility with the resin and improves the toughness and impact resistance substantially. Considerable enhancement of tensile strength is also noticed at about 5% by weight of epoxidized novolac resin. TGA, DMA, and DSC were used to study the thermal properties of the toughened resin and the fracture behavior was studied using SEM. The blends are also found to have better thermal stability. Blending with EPN can be a useful and cost-effective technique for modification of UPR. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 457–465, 2006

Key words: epoxidized phenolic novolac resins; hybrid polymer networks; impact resistance; toughness; unsaturated polyester resin

INTRODUCTION

Unsaturated polyester resins (UPRs) are widely used as a matrix for fiber-reinforced plastics (FRPs). The widespread use of these resins is due to their low cost, ease of processing, excellent wetting properties with reinforcements, good weathering resistance, excellent dimensional stability, and the wide variety of grades available. UPRs are blends of unsaturated polyester with an unsaturated coreactant diluent like styrene. Carothers was the first to prepare UPR with well-defined polymeric structures.¹ The general purpose (GP) grade UPR is a blend of styrene with the condensation product of 1,2-propylene glycol and a mixture of maleic acid and phthalic acid in the form of the anhydride. When crosslinking is initiated, with the help of a catalyst and an accelerator, styrene forms polystyrene chains, which crosslink the polyester chains at the sites of unsaturation.² The cured UPR has high glass transition temperature values and are too brittle for many engineering applications in the absence of reinforcements.³ Although failure in FRP is often limited to the resin–reinforcement interface,⁴ ar-

reas with relatively low amount of fibers are prone to damage when the product is in use or during demoulding.

One major approach towards toughening UPR is the incorporation of elastomers.^{5–8} Notable success has been achieved in this area over the past few decades. The modification of resin, using an elastomer additive, leads to a randomly dispersed rubbery phase in the material. This results in enhanced dissipation of energy before impact failure. Incorporation of elastomers also causes significant reduction in mold shrinkage. It has been found that a significant enhancement in toughness can be obtained by adding thermoplastics.⁹ The solubilized or finely dispersed thermoplastics are precipitated into the interstitial spaces within the crosslinked network, as styrene is depleted from the solution during crosslinking.

Chemical modification using other resins is another possibility. Recently, block copolymers of UPR with polyurethanes, polyureas, polysiloxanes, polyimides, polyoxazolines, or polyglycols have been reported.¹⁰ Another approach is the copolymerization of hydroxyl- or carboxyl-terminated liquid rubbers and polymer monomer units, which result in polyesters containing rubber segments in the main chain.¹¹ Modification of UPR with dicyclopentadiene,¹² bismaleimide,¹³ and poly(-caprolactone)-per fluoro polyethers¹⁴ has also been studied recently. Reactive blending with

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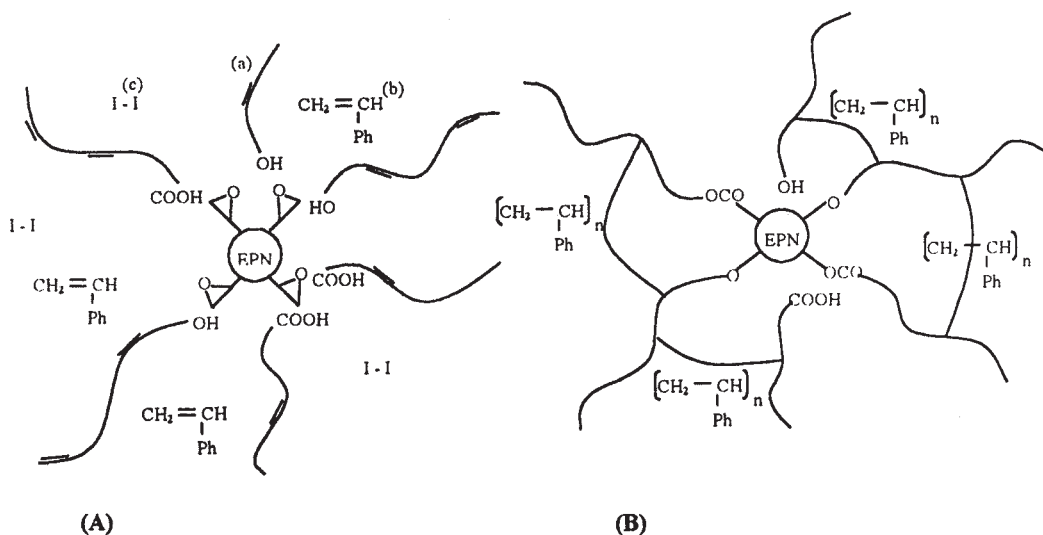


Figure 1 Schematic representation of EPN modified UPR (A) before cure (B) after cure: (a) UPR, (b) styrene, and (c) initiator.

other thermoset resins offers another attractive route and can lead to deactivating the end groups of UPR.¹⁵

Reactive blending

In recent years, chemical modification by reactive blending of UPR and other thermosets via semi-interpenetrating polymer networks and hybrid polymer networks (HPNs) has been reported. Blending of epoxy resin and polyesters resulting in IPNs¹⁶⁻¹⁸ has been widely studied. HPNs of polyurethane prepolymers and unsaturated polyester are also reported.¹⁹⁻²² Segmented polyester polyurethanes have been studied by Cooper and coworkers.^{23,24} Similarly, creation of chemical bonds between elastomer and UPR, using methacrylate end-capped carboxy terminated nitrile rubber²⁵ or isocyanate end-capped polybutadiene²⁶ or epoxy terminated nitrile rubber,²⁷ has also been explored. The mechanical properties of resins and laminates are improved by this technique.

In this investigation, epoxidized phenolic novolac resin has been used as a modifier for UPR. To our knowledge this is the first study of this type involving EPN. The blends are highly compatible and have a shelf life of at least 6 months. The hydroxyl and carboxyl end groups of UPR or unreacted anhydrides can open the epoxy rings of the EPN at the peak exothermic temperature attained during the cure of polyester resin. This can lead to the formation of hybrid networks of EPN and UPR with idealized structures shown in Figure 1.

EXPERIMENTAL

Materials

GP grade UPR (Bakelite Hylam resin HSR 8113M), methyl ethyl ketone peroxide (catalyst) and cobalt

naphthenate (accelerator) were supplied by Sharon Engineering Enterprises (Cochin, India). Phenol, *p*-cresol, sodium hydroxide, formaldehyde, and epichlorohydrin were supplied by E. Merck India Ltd. (Bombay, India).

Preparation of epoxidized phenolic novolacs

The novolacs were first prepared by reacting phenol with formaldehyde in presence of oxalic acid catalyst in a three-necked flask fitted with a mechanical stirrer, water condenser, and thermometer. The reaction mixture was heated and allowed to reflux at about 100°C for 2-3 h. When the resin separated from the aqueous phase the reaction was stopped. The resin was neutralized with sodium hydroxide, filtered, washed with

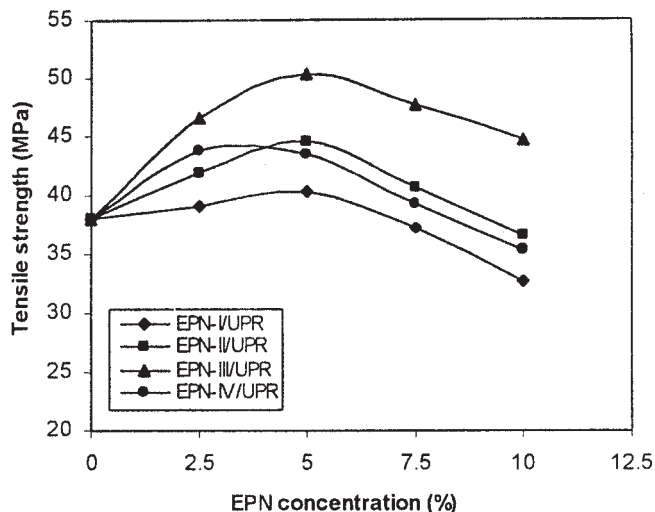


Figure 2 Tensile strength of modified resin versus EPN concentration.

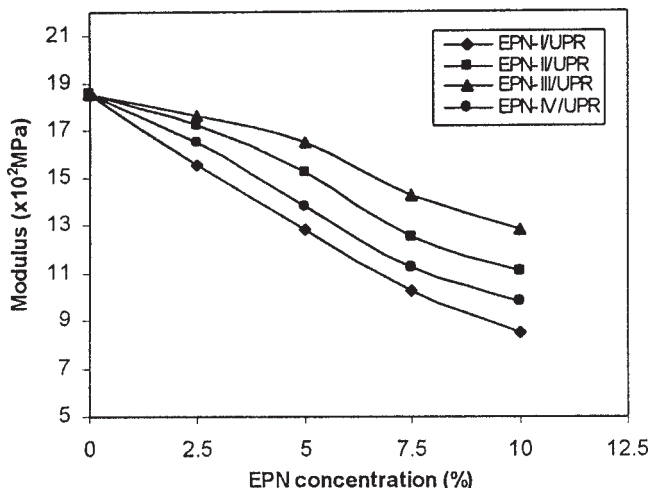


Figure 3 Tensile modulus of modified resin versus EPN concentration.

water, and vacuum dried. The novolac resin contains 4–6 benzene rings per molecule.³

Epoxidized phenolic novolac resin was prepared by the following method. About 1 mol of the novolac resin was dissolved in 8 mol of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 16 h, while 4 mol of 30% sodium hydroxide solution was added drop wise. The rate of addition was maintained such that the reaction mixture remained at a pH, insufficient to color phenolphthalein. The resulting organic layer was separated, dried with sodium sulfate, and then fractionally distilled under vacuum. The epoxide equivalent was determined by reacting a known quantity of resin with hydrochloric acid in pyridine medium and measuring the unreacted acid by back titration with standard alkali.²⁸

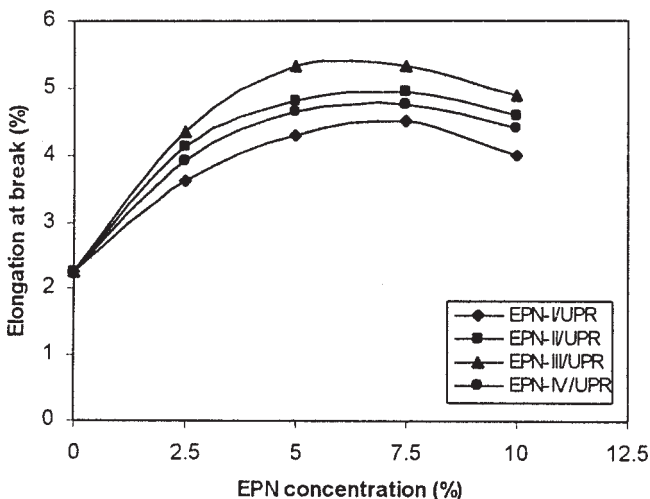


Figure 4 Elongation at break of modified resin versus EPN concentration.

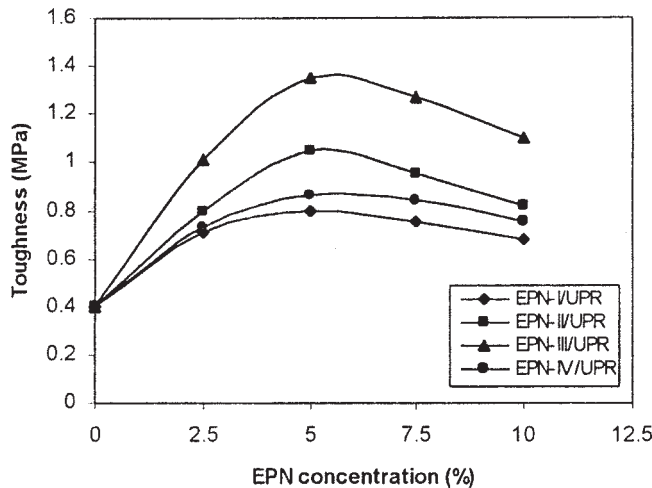


Figure 5 Toughness of modified resin versus EPN concentration.

Various stoichiometric ratios (1 : 0.6, 1 : 0.7, 1 : 0.8, and 1 : 0.9) of phenol and formaldehyde were employed for the preparation of the novolac resin. The corresponding EPNs are designated as I, II, III, and IV. The weight per epoxy (wpe) values of these EPNs are 181.8, 175, 169.5, and 204, respectively.

Modification of UPR by EPNs

For comparison purposes the unmodified resin was first cured at room temperature by a catalyst (methyl ethyl ketone peroxide as 60% solution in dimethyl phthalate) and accelerator (6% solution of cobalt naphthenate in styrene) combination. These were used in concentrations of 0.5 and 1% of the weight of the resin respectively. The resin was then poured into appropriate molds coated with a releasing agent. Cur-

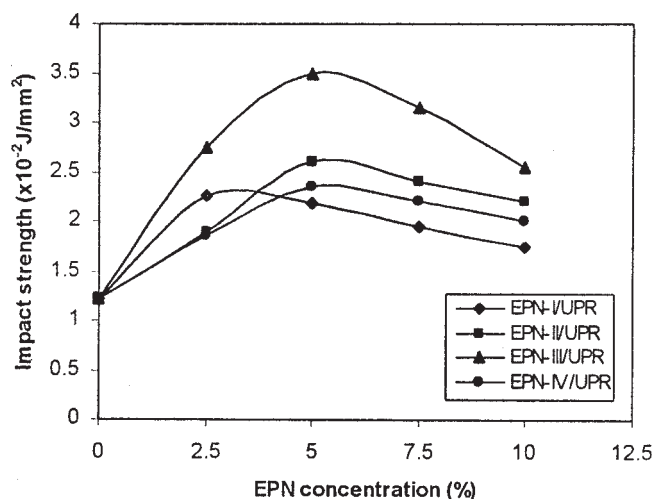


Figure 6 Impact strength of modified resin versus EPN concentration.

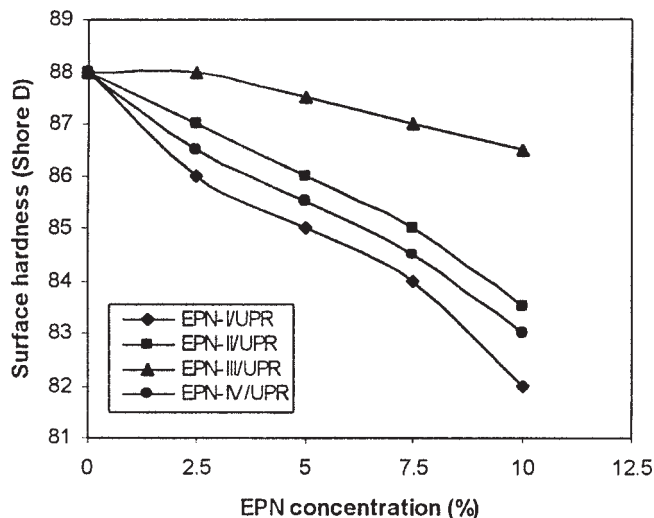


Figure 7 Surface hardness of modified resin versus EPN concentration.

ing was done at room temperature for 24 h followed by post curing at 80°C for 3 h in an air oven.

Varying amounts (0–10 wt %) of EPNs were added to the resin. The mixture was stirred well to give a homogeneous liquid. Curing and post curing of the blend was done by the same procedure employed for UPR.

The samples, after post curing, were tested for tensile strength, modulus, elongation at break, toughness, impact strength, surface hardness, abrasion resistance, and water absorption, taking six trials in each case. The tensile properties were tested on a Shimadzu Autograph Universal Testing Machine (ASTM D638–89) and Izod impact strength was measured on a Zwick impact tester as per ASTM D256 specifications. A shore D Durometer was used for measuring surface

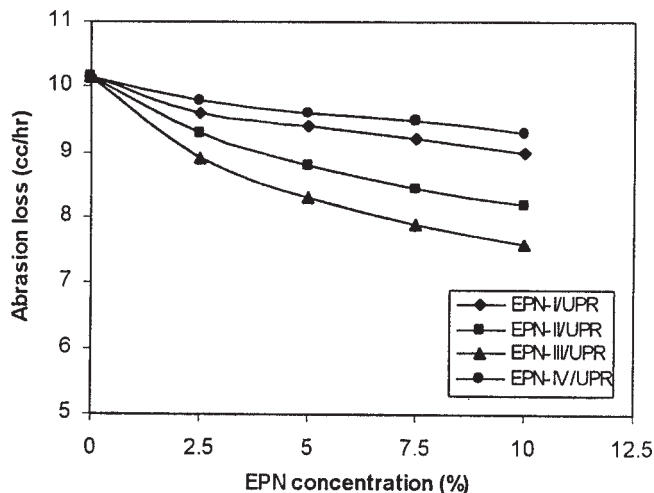


Figure 8 Abrasion loss of modified resin versus EPN concentration.

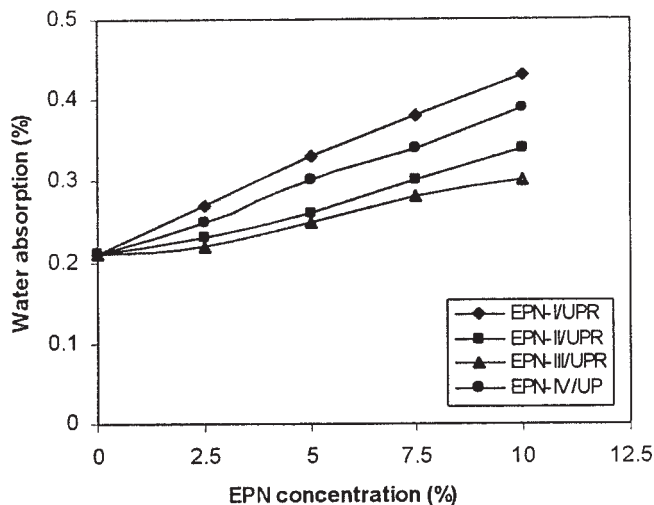


Figure 9 Water absorption of modified resin versus EPN concentration.

hardness (ASTM D2240–86). Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55,516. Water absorption was tested as per ASTM D570. The scanning electron micrographs (SEM) of the fracture surfaces of unmodified and modified UPR were taken on a Cambridge Instruments S 360 Stereoscanner Version V02–01. A TA Instruments' TGA Q 50 was used to investigate thermal degradation. TA Instruments DSC Q 100 equipped with a RCS cooling system was used to study thermal transitions in the samples (at 10°C/min). The damping qualities were measured using fixed frequency dynamic analysis techniques. A dynamic analyzer model DMA-983 from DuPont, USA, was used for this purpose. DMA test were conducted at a constant frequency of 1 Hz. A temperature ramp was run from room temperature to 200°C at 1°C/min to get an overview of the thermomechanical behavior of modified and unmodified samples.

Soxhlet extraction of cured resin samples using benzene was done for 48 h to determine the amount of soluble matter. Samples for spectral studies were prepared by casting films and subsequently extracting them with benzene to remove any unreacted material. The crosslink density was indirectly estimated from the equilibrium swelling data using chloroform. The volume fraction of polyester (V_p) in the swollen samples was calculated.²⁹ V_p is linearly related to the crosslink density of the polymer samples.

RESULTS AND DISCUSSION

EPN can influence UPR properties by causing chain extension or crosslinking. HPNs are thus formed. The hydroxyl and carboxyl end groups in UPR catalyzes the curing reactions of EPN resulting in linking of two or more UPR chains. Considerable improvement in

TABLE I
Summary of Properties of UPR Modified With 0–10% Epoxy Resins

Property	UPR	Maximum improvement achieved (%) / epoxy resin concentration (%)				
		EPN-I/UPR	EPN-II/UPR	EPN-III/UPR	EPN-IV/UPR	DGEBA/UPR
Tensile strength (MPa)	38	5.92/5	17.11/5	32.24/5	15.13/2.5	26.32/7.5
Modulus (MPa)	1850	-16.22/2.5	-6.76/2.5	-4.59/2.5	-10.70/2.5	-7.03/2.5
Elongation at break (%)	2.25	100/7.5	120/7.5	136.4/7.5	111/7.5	100/7.5
Toughness (MPa)	0.4	100/5	162.5/5	237.5/5	115/5	175/7.5
Impact strength (10^{-2} J/mm ²)	1.21	87.5/2.5	116.67/5	189.26/5	95.83/5	119/7.5
Hardness (Shore D)	88	-2.27/2.5	-1.14/2.5	0/2.5	-1.7/2.5	-0.56/2.5
Abrasion loss (cc/hr)	10.15	-5.42/2.5	-8.37/2.5	-12.31/2.5	-3.44/2.5	-2.46/2.5
Water absorption (%)	0.21	104.76/10	61.9/10	42.86/10	85.71/10	61.9/10

TABLE II
Soxhlet Extraction and Swelling Data

Property	UPR	EPN-I/UPR	EPN-II/UPR	EPN-III/UPR	EPN-IV/UPR	DGEBA/UPR
5 % Epoxy resin						
Soluble matter (%)	9.02	6.42	5.85	4.60	5.70	5.42
V_p	0.92	0.936	0.942	0.964	0.953	0.95
10 % Epoxy resin						
Soluble matter (%)	9.02	6.81	6.21	4.82	6.12	5.85
V_p	0.92	0.931	0.938	0.958	0.947	0.945

mechanical properties is noticed after this. Possible reasons for property enhancement are chain extension and hybrid network formation. The results of earlier studies based on addition of commercial epoxy resin (DGEBA) to UPR are also included here for comparison.

Physical properties

Tensile properties

The effect of addition of various EPNs on the tensile properties is shown in Figure 2–4, which indicate the variation in tensile strength, modulus, and elongation at break, respectively. In Figure 2, tensile strength values obtained by adding EPN-III are significantly higher than that obtained by adding other EPNs. Tensile strength reaches a maximum at 5% EPN concentration on adding progressively larger amounts of EPN. Beyond this point, addition of more EPN results in lowering of tensile strength. The improvement in tensile strength over that of the base resin at all percentages of EPN-III is due to its greater functionality as indicated by lower wpe values. Tensile strength values in the case of EPN-I, EPN-II, and EPN-IV are lower, presumably due to their lower epoxy functionality. All the EPNs are seen to improve the tensile strength to varying extents at low concentrations due to the formation of hybrid networks. At higher percentages, many epoxy groups of EPN may remain unopened resulting in weakening of the matrix.

Figure 3 shows the effect of EPNs on tensile modulus. Modulus values are lower than the base resin values at all concentrations. Modulus decreases steadily on adding progressively larger amounts of EPN. This reflects the capacity of the modified resin to absorb energy and provide a higher degree of molecular flexibility.

The effect of EPN addition on the elongation at break is shown in Figure 4. Compared with unmodified resin the blends show substantial increase in elongation. Blends show maximum elongation at 7.5 wt % of epoxy novolac. The addition of EPN-III produces

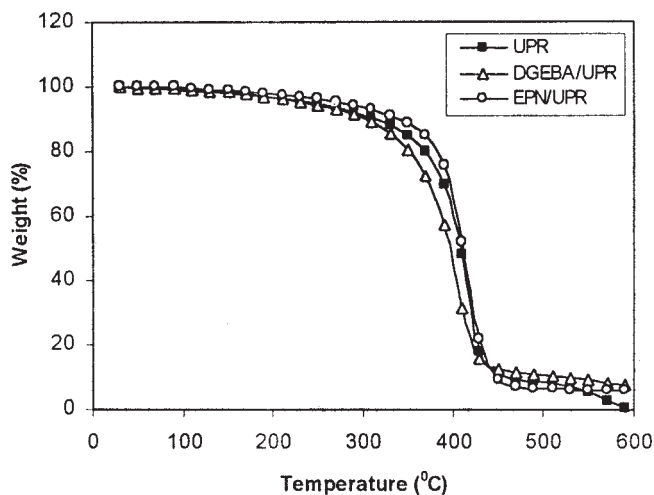


Figure 10 TGA curves of (a) UPR, (b) 5% EPN-III/UPR, and (c) 5% DGEBA/UPR.

TABLE III
Thermal Properties

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
UPR	296.88	412.53	408.98	0.3327
5 %EPN-III/UPR	356.58	414.12	411.32	7.633
5 % DGEBA/UPR	277.19	403.33	396.15	5.707

the greatest increase in elongation at break at about 5–7.5% EPN concentration. The increase in elongation at break can be attributed to the presence of ether linkages as well as straightening of entangled chains.

Toughness properties

The variation in toughness of the cured resin with the EPN content is shown in Figure 5. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement between the chains. The toughness of the blend is maximum at 5% EPN-III concentration (about 338% of the toughness of UPR). At still higher percentages, a weakening of the matrix may result, as a part of the EPN remains unreacted. The toughening effect is less in the case of EPN-I, EPN-II, and EPN-IV because of the lower epoxy values.

Figure 6 shows the variation in impact strength with EPN concentration. In this respect also EPN-III shows maximum improvement again, at a concentration of 5%. This can also be explained in terms of a higher degree of molecular flexibility and greater capacity for spatial molecular rearrangement.

Hardness and abrasion loss

Figure 7 indicates a general lowering of surface hardness on addition of all types of EPNs. This can probably be attributed to higher degree of flexibility. This effect is maximum for EPN-IV and minimum for EPN-III.

There is a decrease in abrasion loss with an increase in EPN concentration for all EPNs (Fig. 8). This may be due to the better compatibility between the resin and EPN and greater cohesion leading to a relatively homogeneous material structure. The abrasion loss of EPN-III is the lowest.

Water absorption

Water absorption of various EPN-modified resins increases steadily, as shown in Figure 9. Increase in water absorption is least in the case of EPN-III. This can be due to a greater extent of chain extension or network formation.

Table I summarizes the effect of adding varying amounts of different EPNs to UPR. The maximum improvement acquired in each property and the cor-

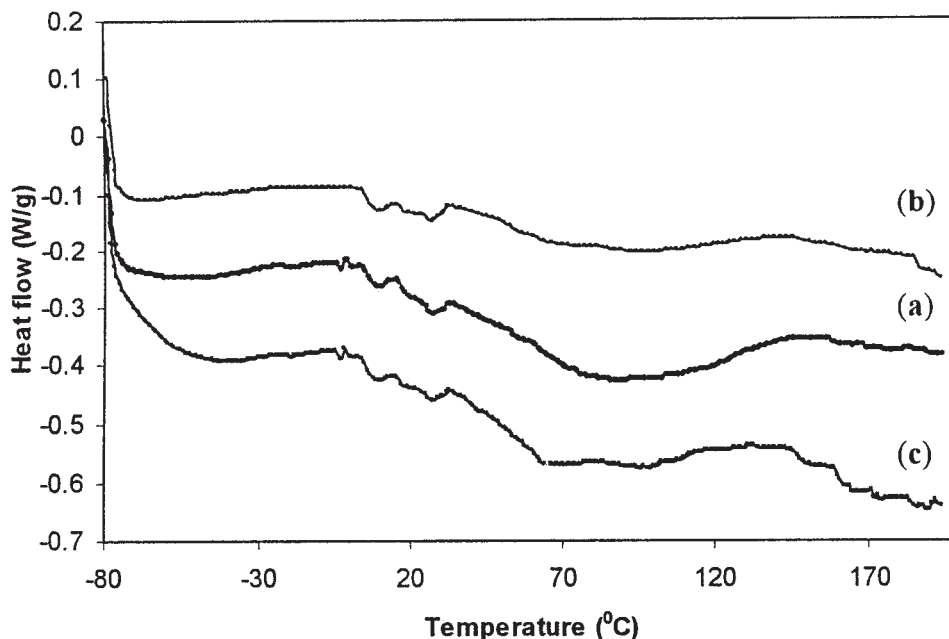


Figure 11 DSC thermograms of (a) UPR, (b) 5% EPN-III/UPR, and (c) 10% EPN-III/UPR.

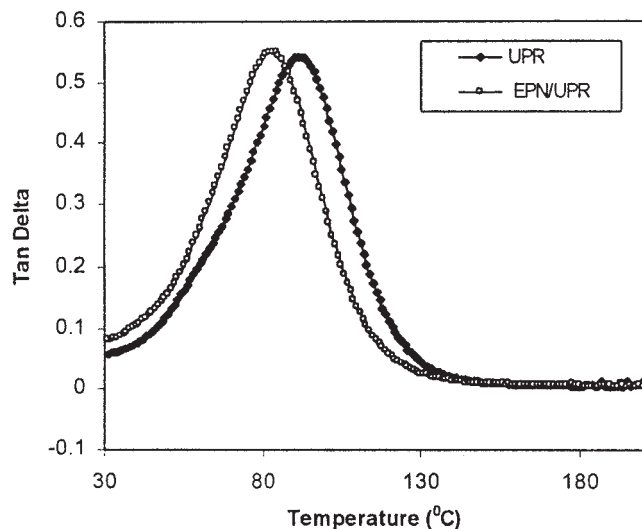


Figure 12 DMA-tan δ curves of (a) UPR and (b) 5% EPN-III/UPR.

responding EPN concentrations are tabulated. It is evident that EPN-III enjoys clear superiority over other EPNs.

Soxhlet extraction and swelling studies

The Soxhlet extraction data (Table II) showed that very little soluble matter could be extracted from epoxy-modified UPR compared with unmodified UPR. This suggests that in this case epoxy compounds form HPNs. The compatibility of epoxy compounds with UPR primarily arises from their polarities. The hydroxyl and carboxyl end groups in the UPR catalyzes the curing reactions of epoxy compounds resulting in interlinking of UPR chains. At 10 wt % EPN, some EPN molecules remain unopened and the extractable matter is slightly higher. The high V_p of modified samples at 5 wt % EPN concentration suggests greater crosslinking. At still higher percentages (10 wt %) V_p shows a marginal decrease because most of the hydroxyl and carboxyl ends of polyester are already used up by the EPN molecules. The unopened epoxy groups create free volumes and enhance the swelling behavior.

Thermal studies

The TGA curves of UPR and its blends with epoxy compounds (5 wt %) are shown in Figure 10. UPR/

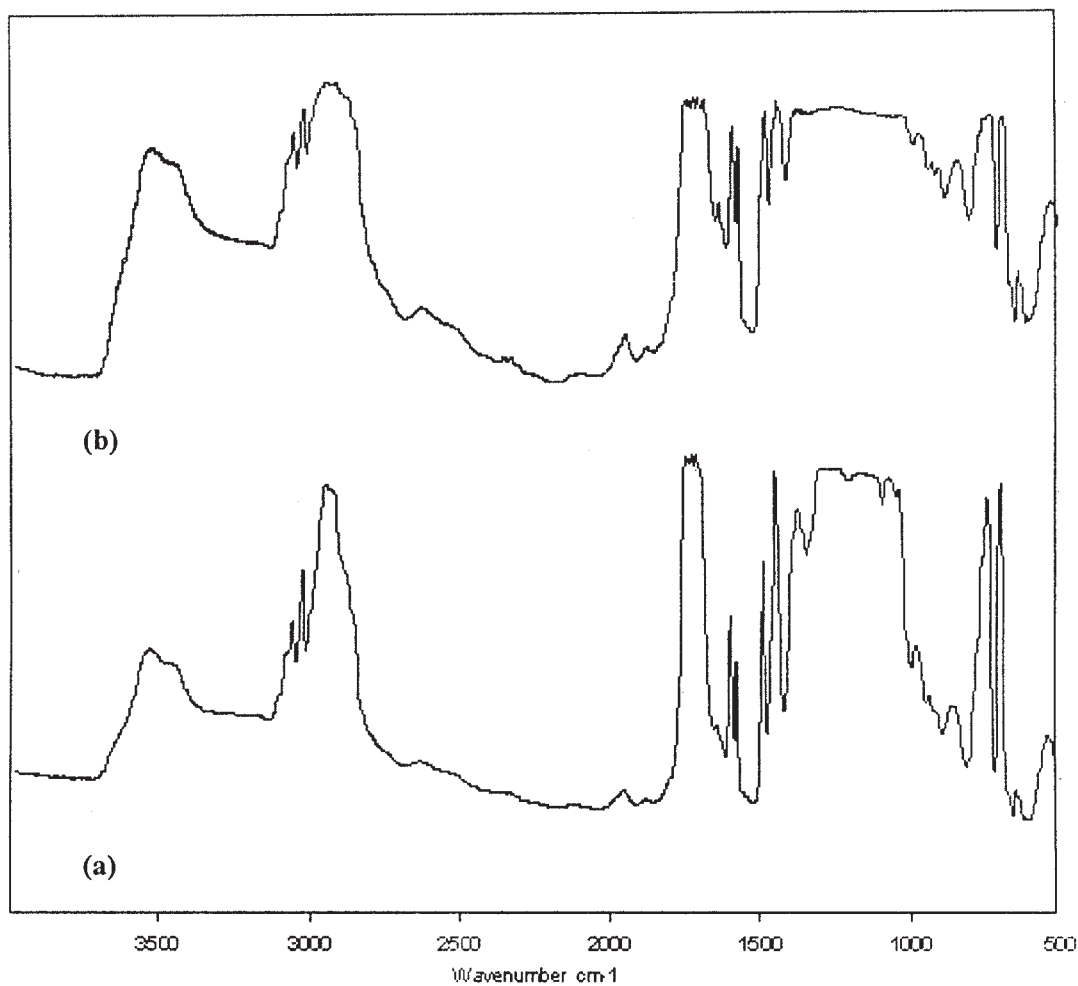


Figure 13 FTIR spectra of (a) UPR and (b) EPN-III/UPR.

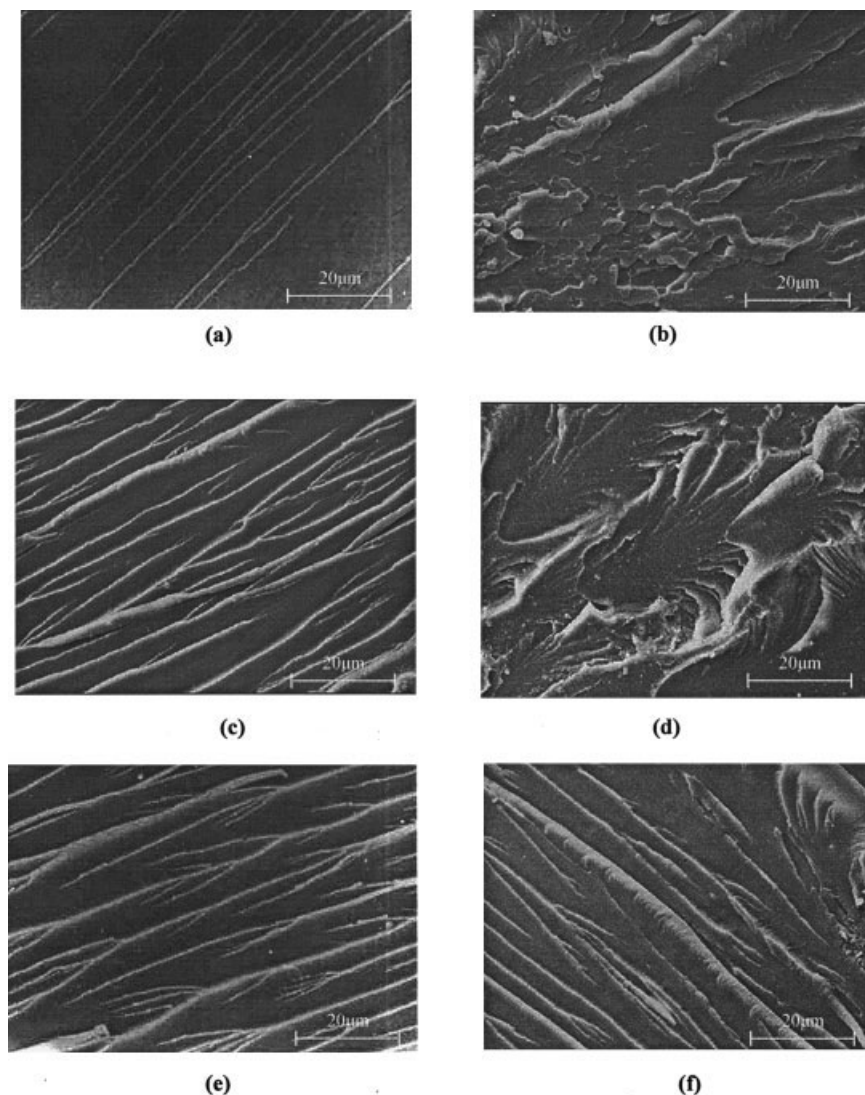


Figure 14 Scanning electron micrographs of fracture surfaces: (a) UPR, (b) EPN-I/UPR, (c) EPN-II/UPR, (d) EPN-III/UPR, and (e) EPN-IV/UPR.

EPN has marginally better thermal stability as shown in Table III.

The DSC curves of UPR and blends with EPN-III are shown in Figure 11. UPR has a T_g of 93°C. Reactive blending with 5% EPN results in a homogeneous HPN with a single T_g (85°C). Addition of 10% EPN exhibits heterogeneity with two T_g 's at 61 and 102°C. Hence it is possible that at higher percentages of EPN, part of the EPN remains unattached to the polyester chain.

T_g values obtained from DMA $\tan \delta$ curves (Fig. 12) for UPR (92°C) and UPR/5% EPN (83°C) are in good agreement with T_g values obtained from DSC curves. The $\tan \delta$ values at 92°C for these polymers are 0.5421 and 0.4495, respectively. The marginal lowering indicates enhanced flexibility.

Spectral studies

Comparing the FTIR spectra of UPR and EPN-III/UPR (Fig. 13), additional peaks at 1243 cm^{-1} correspond to ether linkages formed during epoxide ring opening.

Morphological studies

Scanning electron micrographs of unmodified and modified UPR fractured at low deformation rate are shown in Figure 14. Referring to the micrograph (a), the fracture path for unmodified resin (UPR) is narrow and continuous indicating rapid crack propagation along the axis of crack growth. The fracture surface is smooth with low ridges and shallow grooves. All the fracture surfaces of the blends are characterized by a morphology in which crazing plays an important part.

EPN-I-modified resin fracture pattern is shown in micrograph (b). This is a low deformation level fracture. Separate ductile deformed films and fibrils are seen. The micrograph of EPN-II-modified resin (c) shows crazes, which represent the initial stage of ductile force fracture. Referring to that of EPN-III modified resin (d), the fracture paths have a feathery texture with large breadth. They are also discontinuous and convoluted. A few peaks and parallel fibril structures in pulled up wavy crest point to the stretching that takes place prior to fracture. Extensive stress whitening is also observed. High toughness and load bearing characteristics are indicated. Micrograph of EPN-IV-modified resin (e) shows fracture paths narrower than those for EPN-III. The ductile fracture pattern is largely retained. DGEBA-modified resin fracture pattern is shown in micrograph (f). Peak structures and fibrils characteristic of ductile fracture is seen. EPN-III shows a clear superiority from the viewpoint of energy absorption, as evidenced by SEM.

CONCLUSIONS

Unlike rubbers, EPNs are highly miscible with UPR. EPN-III, the epoxy novolac prepared using a phenol: formaldehyde stoichiometry of 1 : 0.8 is far superior to all other EPNs considered in this investigation for modifying the properties of UPR. Toughness and tensile properties show maximum improvement at about 5 wt % EPN concentration. In the case of EPN-III, the tensile strength of the cured UPR has been found to increase by as much as 32% simultaneously improving the toughness by about 238%. The improvement in toughness and impact resistance has been achieved without seriously affecting other properties. Considering the low percentages of EPN required and the stability of the mixtures, this method of modification has considerable practical significance.

References

- Carothers, W. H. *J Am Chem Soc* 1929, 51, 2569.
- Boeing, H. V. *Unsaturated Polyester*; Elsevier: New York, 1964.
- Bryson, J. A. *Plastic Materials*; Butterworths: Heinemann, Oxford, 1999.
- McGarry, F. J. *Rubber in Crosslinked Polymers*; Applied Science: London, 1983.
- Owen, M. J.; Rose, R. G. *J Mater Sci* 1975, 10, 1711.
- Christiansen, A.; Shortall, J. B. *J Mater Sci* 1976, 11, 1113.
- Leel, L.; Riew, C. K.; Seeber, A. R. *Polym Mater Sci Eng* 1990, 6, 63.
- Laurent, S.; Yeong, S. Y.; Pascault, J.-P. In *Rubber Toughened Plastics*; Keith Riew, C., Kinloch, A. J., Eds.; *Advances in Chemistry Series*, Vol. 233; American Chemical Society: Washington, DC, 1993.
- Yee, A. F.; Du, J.; Thouless, M. D. *Polymer blends—Performance*, Vol. 2; Paul, D. R., Bucknall, C. B., Eds.; John Wiley: New York, 1999.
- Keith Riew, C. *Rubber Toughened Plastics*; *Advances in Chemistry Series*, Vol. 222; American Chemical Society: Washington, DC, 1989.
- Rosa, V. M.; Jozsef, K.-K.; Felisberti, M. I. *J Appl Polym Sci* 2001, 81, 3280.
- Chiu, H. T.; Chen, S. C. *J Polym Res* 2001, 8, 183.
- Gawdzik, B.; Matynia, T.; Chmielewska, E. *J Appl Polym Sci* 2001, 82, 2003.
- Messori, M.; Toselli, M.; Pilati F.; Tonelli, C. *Polymer* 2001, 42, 09877.
- Kim, D. S.; Cho, K.; An, J. H.; Park, C. E. *J Mater Sci* 1994, 29, 1854.
- Lin, M.-S.; Chang, R.-J.; Yang, T.; Shih, Y.-F. *J Appl Polym Sci* 1995, 55, 1607.
- Lin, M.-S.; Liu, C.-C.; Lee, C.-T. *J Appl Polym Sci* 1997, 65, 1525.
- Shaker, Z. G.; Browne, R. M.; Stretz, H. A.; Cassidy, P. E.; Blanda, M. T. *J Appl Polym Sci* 2002, 84, 2283.
- Chou, Y. C.; Lee, L. J. *Polym Eng Sci* 1994, 34, 1239.
- Chou, Y. C.; Lee, L. J. *Polym Eng Sci* 1995, 35, 976.
- Valette, L.; Hsu, C.-P. *Polymer* 1999, 40, 2059.
- Xu, M. X.; Xiao, J. S.; Zhang, W. H.; Yao, K. D. *J Appl Polym Sci* 1994, 54, 1659.
- Srichatrapimuk, V. W.; Cooper, S. L. *J. Macromol Sci B Phys* 1978, 15, 267.
- Van Bogart, J. W. C.; Lilaonitkul, A.; Cooper, S. L. *Adv Chem Ser* 1979, 176, 3.
- McGarry, F. J.; Rowe, E. H.; Riew, C. K. *Polym Eng Sci* 1978, 18, 2.
- Malinconico, M.; Martuscelli, E.; Ragosta, G.; Volpi, M.G. *Int J Polym Mater* 1987, 11, 317.
- Crosbie G. A.; Phillips, M. G. *J Mater Sci* 1985, 20, 182.
- Jadhav, J. Y.; Kantor, S. W. In *Encyclopedia of Polymers Science and Engineering*, 3rd ed, Vol. 12; Mark, H. F., Bikales, N. M., Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1990.
- Brown, R. *Handbook of Polymer Testing*; Marcel Dekker: New York, 1999.