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Epoxy-modified, unsaturated polyester hybrid networks

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Abstract

Hybrid polymer networks (HPNs) based on unsaturated polyester resin (UPR) and epoxy resins were synthesized by reactive blending. The epoxy resins used were epoxidised phenolic novolac (EPN), epoxidised cresol novolac (ECN) and diglycidyl ether of bisphenol A (DGEBA). Epoxy novolacs were prepared by glycidylation of the novolacs using epichlorohydrin. The physical, mechanical, and thermal properties of the cured blends were compared with those of the control resin. Epoxy resins show good miscibility and compatibility with the UPR resin on blending and the co-cured resin showed substantial improvement in the toughness and impact resistance. Considerable enhancement of tensile strength and toughness are noticed at very low loading of EPN. Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were employed to study the thermal properties of the toughened resin. The EPN/UPR blends showed substantial improvement in thermal stability as evident from TGA and damping data. The fracture behaviour was corroborated by scanning electron microscopy (SEM). The performance of EPN is found to be superior to other epoxy resins.

Keywords: Epoxidised phenolic novolac resins; Epoxidised cresol novolac resins; Hybrid polymer networks; Impact resistance; Toughness; Unsaturated polyester resin

1. Introduction

Unsaturated polyester resins (UPR) are one of the important thermosetting materials used for the fabrication of glass-reinforced plastics and polymeric composites. The widespread use of these resins is due to their relatively low cost, ease of processing, excellent wetting properties with reinforcements, good balance of properties and the wide variety of grades available. UPR are solutions of unsaturated polyester with an unsaturated co-reactant diluent like styrene. Carothers was the first to prepare UPR with well-defined polymeric structures. The general purpose (GP) grade UPR is a blend of styrene with the condensation product of 1,2 propylene glycol with a mixture of maleic acid (MA) and phthalic acid in the form of the anhydride. When cross-linking is initiated with the help of a catalyst and an accelerator, styrene forms polystyrene chains, which cross-link the polyester chains at the sites of unsaturation. The highly

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cross-linked three-dimensional molecular structure of the cured resin gives high stiffness, strength, enhanced glass transition temperature and good heat and solvent resistance. However, they suffer from a major drawback namely, brittleness and poor resistance to crack propagation [1]. Although failure in fibre reinforced plastic (FRP) is often limited to the resin-reinforcement interface [2], areas with relatively low amount of fibres are prone to damage when the product is in use or during demoulding.

UPR are blended with several substances to improve their impact strength and fracture properties. These additives should be miscible in the uncured resin, and get phase separated during curing. The degree of toughening is strongly dependent on the phase-separated morphology [3]. It also depends on the type and proportion of the two components, shape, connectivity and size of the domains [4]. A fine dispersion of elastomer in the UPR matrix and strong adhesion between the matrix and dispersion is desirable. The miscibility and interfacial properties of the additive/resin blends play important roles in the toughening process [5]. The modification of resin, using elastomer additive leads to a randomly dispersed rubbery phase in the material, and helps to dissipate energy for imparting impact resistance. Modification by blending with thermoplastic low profile additives [6] is another possibility. The solubilised or finely dispersed thermoplastics are precipitated into the interstitial spaces within the cross-linking network as styrene is depleted from the solution during cross-linking.

Recently, block copolymers that contain UPR with polyurethanes, polyureas, polysiloxanes, poly- imides, polyoxazolines, or polyglycols have been reported [5]. Another approach is the copolymerisation of hydroxyl or carboxyl terminated liquid rubbers or polyethylene glycols with UPR monomer units [7]. This results in polyesters containing rubber or polyethylene glycol segments in the main chain. Modification of UPR with dicyclopentadiene [8] and bismaleimide [9] has also been reported recently. Reactive blending of UPR with other thermosets is another possibility.

Reactive blending with thermoset resins can lead to deactivating the end groups of UPR chains. In recent years, chemical modification by reactive blending of UPR and other thermosets via semi interpenetrating polymer networks (IPNs) and hybrid polymer networks (HPNs) has been reported. Blending of epoxy resin and polyesters resulting in IPNs [10–13] has been extensively studied. An intercrosslinked network of unsaturated polyester-bismaleimide modified epoxy matrix systems was developed [14]. Interpenetrating networks of varying percentages of bismaleimide in vinyl ester oligomer modified unsaturated polyester matrixes have been developed [15]. Hybrid polymer networks of polyurethane prepolymers and unsaturated polyester are also studied [16–21]. Similarly, chemical bonding between elastomer and UPR using methacrylate end-capped nitrile rubber or epoxy-terminated nitrile rubber (ETBN) or isocyanate end-capped polybutadiene is an attractive route [22]. The mechanical properties of resins and laminates are improved by this technique.

The main objective of this investigation is to study the modifying effect of epoxidised novolac resins on UPR. In the present study, HPNs based on unsaturated polyester and epoxidised novolac resins have been prepared by reactive blending. Epoxidised novolac resins used are epoxy phenol novolac resins (EPNs) and epoxy cresol novolac resins (ECNs). The blends of epoxidised novolac resin with UPR are highly compatible and have a shelf life of at least 6 months. For comparison purposes similar blends of commercial epoxy resin (DGEBA) with UPR are also prepared and properties evaluated. The impact of matrix modification on mechanical, thermal and fracture properties has been examined. To our knowledge, no such a technique has been used for polyester toughening.

2. Experimental

2.1. Materials

General purpose grade UPR (Bakelite Hylam, Hyderabad, India, HSR 8113 M), commercial DGEBA (Athul Polymers India Ltd., Gujarat, India, 103 grade, weight per epoxy [wpe] = 188), methyl ethyl ketone peroxide (catalyst) and cobalt napthenate (accelerator) were supplied by Sharon Engineering Enterprises, Cochin, India. Phenol, *p*-cresol, sodium hydroxide, formaldehyde and epichlorohydrin were supplied by E. Merck India Ltd, Mumbai, India. EPN 1138 (Araldite, wpe = 178) was obtained from Vantico Performance Polymers Pvt. Ltd., Mumbai, India.

2.2. Preparation of epoxidised novolac resin

Novolacs were based on both phenol and cresol. They were prepared by reacting phenol/cresol with formaldehyde in the molar ratio of 1:0.8 in presence of oxalic acid catalyst in a 3-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 neutralised with sodium hydroxide, filtered, washed with water and vacuum dried. The novolac resin contains 4–6 benzene rings per molecule [1].

One mole of the above 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 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 epoxide equivalent was determined by reacting a known quantity of resin with hydrochloric acid and measuring the unreacted acid by back titration with standard alkali [24]. The wpe values of EPN and ECN are 169.5 and 176, respectively. The Fourier transform infrared (FTIR) spectrum of synthesised EPN was taken.

2.3. Modification of UPR with epoxy resins

Unmodified resin was first cured at room temperature by a catalyst (methyl ethyl ketone peroxide dissolved in dimethyl phthalate containing 60% peroxide) and accelerator (6% solution of cobalt napthenate in styrene) combination. These were used in concentrations of 1% and 0.5% of the weight of the resin, respectively. The resin was then poured into appropriate moulds coated with a releasing agent. Curing was done at room temperature for 24 h followed by post curing at 80 °C for 3 h in an air oven.

The blends with EPN, ECN and DGEBA were prepared by the following procedure. Varying amounts (0–10 wt%) of these modifiers were added to the resin. The mixture was stirred well to give a homogeneous liquid. Curing and post curing of the blend was done as per the procedure employed for UPR.

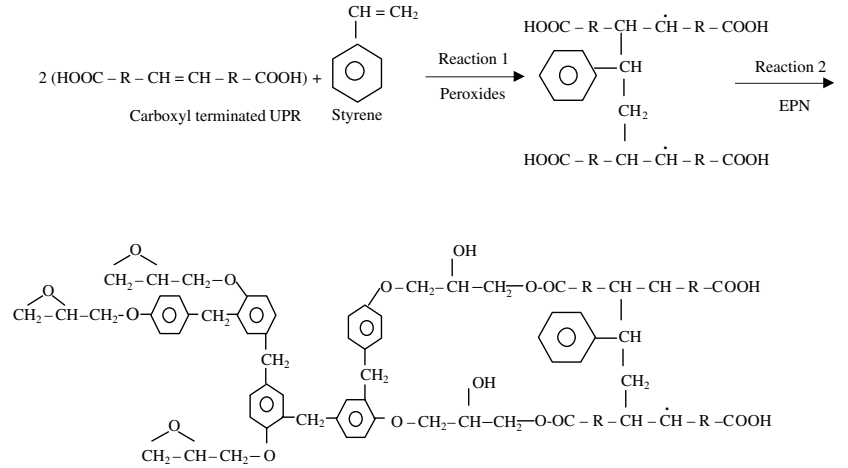
2.4. Testing methods

The FTIR spectrum of UPR and EPN/UPR blends were taken. Samples for spectral studies were prepared by casting films and subsequently extracting them with benzene to remove any unreacted material. Soxhlet extraction of cured resin samples was done using benzene for 48 h to determine the amount of unreacted epoxy/polyester resins. The cross-link density was indirectly estimated from the equilibrium swelling data. The volume fraction of polyester (V_p) in the swollen samples was calculated [25]. V_p is a measure of the extent of cross-linking of the polymer samples.

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 6 trials in each case. The tensile properties were tested 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. A shore D Durometer was employed for measuring surface hardness (ASTM D 2240-86). Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55516. Water absorption was tested as per ASTM D 570. 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 a heating rate of 10 °C/min. The damping properties were measured using fixed frequency dynamic mechanical analysis techniques. A dynamic analyser model DMA-983 from Dupont, USA was made use of 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. The SEM micrographs of the fracture surfaces of unmodified and modified UPR were taken in a Cambridge Instruments S 360 Stereoscanner-Version V02-01.

3. Results and discussion

HPNs based on unsaturated polyester and epoxidised novolac resins are formed by reactive blending. The hydroxyl and carboxyl end groups of UPR or the unreacted anhydrides can open the epoxy rings of the epoxy resin at the peak exothermic temperature attained during the cure of polyester resin. One possible hybrid polyester/EPN reaction is shown below:



This can lead to the formation of HPNs of epoxy novolac resins and UPR with idealised structures as shown in Fig. 1 [23].

3.1. Spectral studies

The peaks at 1236.9 and 915 cm^{-1} in the FTIR spectrum of the synthesised EPN (Fig. 2) denotes epoxide linkage. Comparing the FTIR spectra of UPR and EPN /UPR (Fig. 3), additional peaks at 1243 cm^{-1} correspond to ether linkages formed during epoxide ring opening.

3.2. Soxhlet extraction and swelling studies

The Soxhlet extraction data (Table 1) showed that the extractable matter diminishes upon reaction with epoxy. One reason is the enhancement of crosslinking and another is the participation of low molecular weight polyester fraction in the reaction with epoxy. Clearly, epoxy resins form hybrid polymer networks by interlinking of the two polymer chains. The compatibility of epoxy resins with UPR primarily arises from their polarities. The hydroxyl and carboxyl end groups in the UPR catalyses the curing reactions of epoxy resins resulting in chain extension and increased crosslinking. The reactive blending is further confirmed by the high V_p of modified samples during swelling studies.

3.3. Mechanical properties

3.3.1. Tensile properties

Referring to Fig. 4 tensile strength values obtained by blending UPR with epoxy resins are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 5-wt%

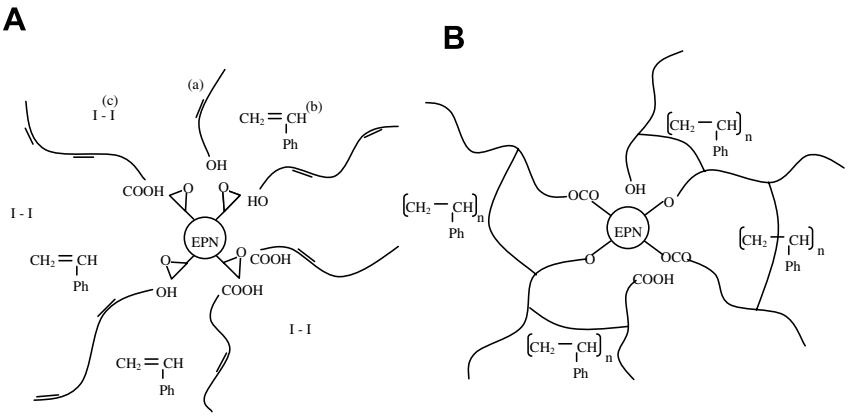


Fig. 1. Schematic representation of EPN modified UPR (A) before cure, (B) after cure (a) UPR, (b) styrene, (c) initiator.

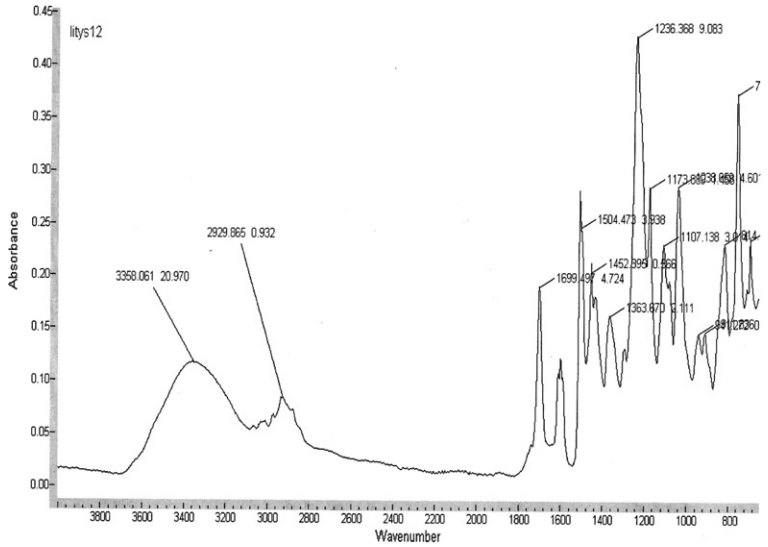


Fig. 2. FTIR spectrum of synthesised EPN.

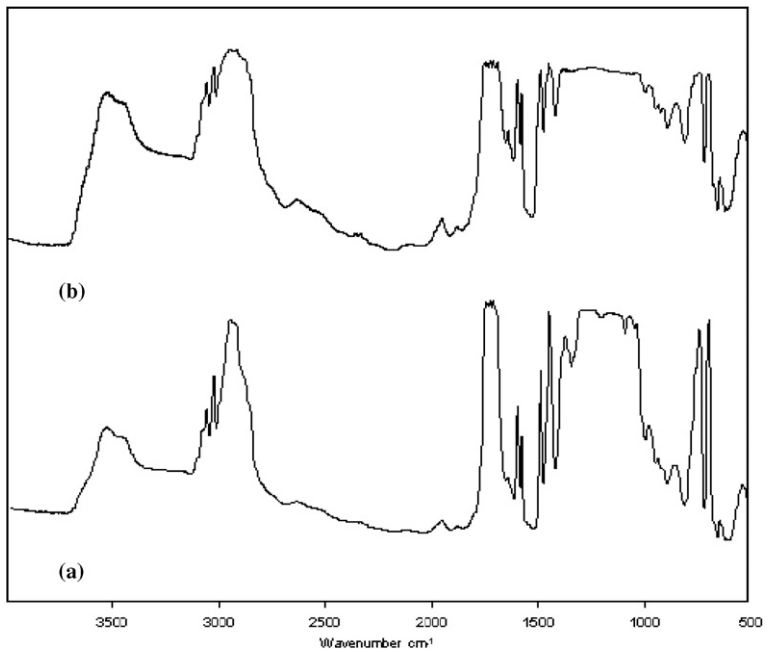


Fig. 3. FTIR spectra of (a) UPR and (b) EPN/UPR.

Table 1
Soxhlet extraction data-epoxy modifier (5 wt%)

Property	UPR	DGEBA/UPR	EPN/UPR	ECN/UPR	EPN-1138/UPR
Soluble matter (%)	9.0	5.4	4.6	6.6	5.7
V_p	0.90	0.95	0.96	0.94	0.94

of epoxy. Further addition causes a decrease in property. The improvement in tensile strength over that of the base resin is due to a higher degree of cross-linking by the interpenetration of networks and chain extension. At higher percentages, many epoxy chains may go uncross-linked, and this leads

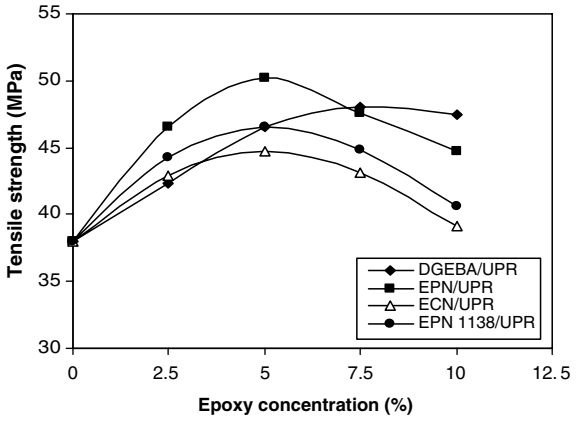


Fig. 4. Tensile strength of modified resin versus epoxy concentration.

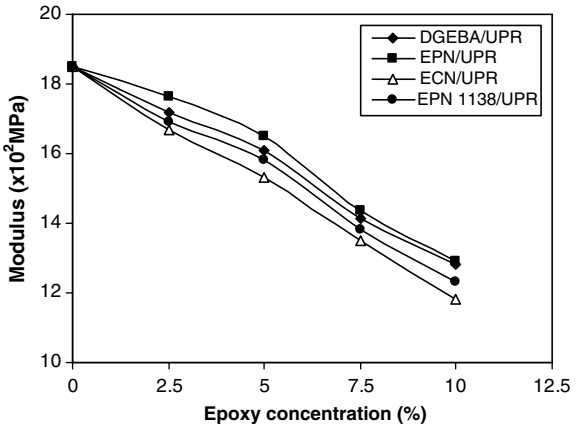


Fig. 5. Tensile modulus of modified resin versus epoxy concentration.

to a plasticising effect and thus weakening the matrix. The greater improvement in tensile strength of EPN over other epoxy resins considered is presumably due to the greater epoxy functionality of EPN. Due to its linear nature and lower functionality, the maximum strengthening takes place at a higher concentration (at 7.5-wt%) in the case of DGEBA. ECN from its relatively more linear configuration is expected to impart good plastic deformation to the matrix and there by enhance the properties of the brittle UPR. However, its more hydrophobic nature (due to alkyl group) and its spatial conformation (in contrast to EPN which is more unsymmetrical and polar) render it less effective in property amelioration.

Fig. 5 shows the effect of epoxy resins on the tensile modulus. The moduli of epoxy blends are lower than that for the neat resin. This reflects the capacity of the modified resin to absorb energy and provide a higher degree of molecular flexibility. This can be attributed to the creation of free volumes within the polymer by virtue of residual epoxy groups originating from epoxy compounds. The reduction in modulus is minimum for EPN and maximum for ECN due to the rigidity of the former and linear nature of the latter.

The effect of addition of epoxy resins on elongation-at-break is given in Table 2. Compared to unmodified resin the blends show substantial increase in elongation. Epoxy blends show maximum elongation at 5–7.5 wt% of epoxy compound. The higher elongation may be the result of entanglement of chains and/or loose packing of the chains arising from uncross-linked epoxy groups. Beyond 7.5%, many epoxy groups of EPN may remain unopened resulting in weakening of the matrix and lowering of elongation-at-break and strength.

3.3.2. Toughness properties

The variation in toughness of the cured resin with epoxy content is shown in Fig. 6. The toughness of the blend is maximum at 5% EPN concentration (about 332% of the toughness of UPR). The effect of adding EPN is far superior to all other epoxy modifiers. The enhanced energy absorption can be attributed to the greater level of flexibility of ether linkages,

Table 2
Summary of properties of UPR modified with 0–10 wt% epoxy resins

Property	UPR	Maximum improvement achieved (%)/epoxy concentration (%)			
		DGEBA/UPR	EPN/UPR	ECN/UPR	EPN (1138)/UPR
Tensile strength (MPa)	38	26.3/7.5	32.2/5	17.8/5	22.5/2.5
Modulus (MPa)	1850	−7.0/2.5	−4.6/2.5	−9.7/2.5	−8.7/2.5
Elongation at break (%)	2.3	100/7.5	136.4/7.5	104.4/5	113.3/5
Toughness (MPa)	0.4	175/7.5	237.5/5	157.5/5	177.5/5
Impact strength ($\times 10^{-2}$ J/mm^2)	1.2	119/7.5	189.3/5	148/5	128/5
Hardness (Shore D)	88	−0.6/2.5	0/2.5	−1.1/2.5	−0.6/2.5
Abrasion loss (cm^3/h)	10.2	−2.5/2.5	−12.3/2.5	−7.4/2.5	−5.4/2.5
Water absorption (%)	0.2	61.9/10	42.9/10	90.5/10	76.2/10

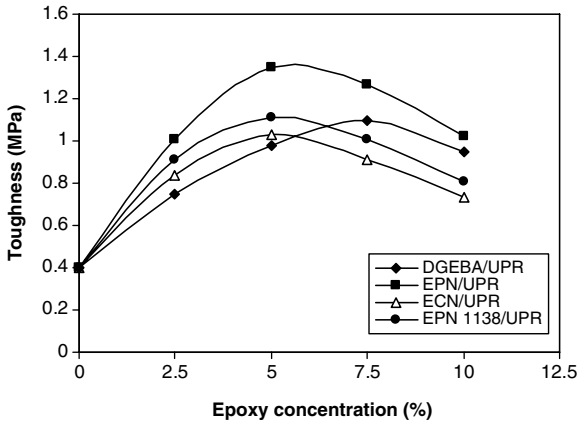


Fig. 6. Toughness of modified resin versus epoxy concentration.

creation of free volumes within the polymer by virtue of residual epoxy groups and capacity for spatial rearrangement of benzene rings. DGEBA, EPN (1138) and ECN have a similar but less pronounced behaviour pattern. The toughening effect is less in these cases due to lower epoxy values and structural differences. Beyond 5-wt%, many epoxy groups of EPN may remain unopened resulting in weakening of the matrix cohesion and lowering of energy absorption.

Impact strength values obtained by blending UPR with epoxy resins are significantly higher compared to that of the unmodified resin (Fig. 7). The

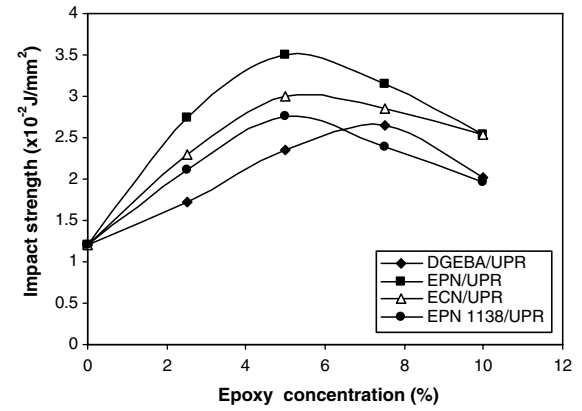


Fig. 7. Impact strength of modified resin versus epoxy concentration.

EPN phase helps to absorb the energy of impact and prevents crack propagation. In this respect also EPN shows maximum improvement again, at a concentration of 5-wt%. This can be attributed to higher degree of molecular flexibility. DGEBA, EPN (1138) and ECN have similar behaviour patterns.

3.3.3. Miscellaneous properties

Table 2 indicates a general lowering of surface hardness on addition of all types of epoxy resins. This is in tune with the reduction in tensile modulus arising from a higher degree of molecular flexibility and the creation of free volumes within the polymer. This effect is maximum for DGEBA and minimum for EPN.

There is a marginal lowering of abrasion loss at low epoxy concentration for all compounds (Table 2). This may be due to compatibility between the UPR resin and epoxy resins and possible inter-chain attractions leading to a relatively homogeneous material structure. Abrasion loss is lowest in the case of EPN.

Water absorption values of various epoxy-modified resins are shown in Table 2. In contract to UPR, epoxy modified resins absorb more water. This is due to increase in the overall polarity of the system and the creation of free volumes within the matrix that can accommodate water molecules. The increase in water absorption is lowest in the case of EPN due to the larger extent of chain extension caused by epoxy groups.

Table 2 summarises the effect of adding varying amounts of different epoxy resins to UPR. The maximum change acquired in each property and the corresponding epoxy concentrations are tabulated. It is evident that EPN enjoys a clear superiority over other epoxy resins considered.

3.4. Thermal studies

UPR/EPN has marginally better thermal stability as shown in Table 3. UPR has a glass transition temperature (T_g) of 93 °C (Fig. 8). Reactive blending with 5% EPN results in a homogeneous HPN with a single T_g (85 °C). Addition of 10% EPN exihibits

Table 3
Thermal properties-TGA epoxy modifier (5 wt%)

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
UPR	297	413	409	0.3
DGEBA/UPR	277	403	396	5.7
EPN/UPR	356	414	411	7.6

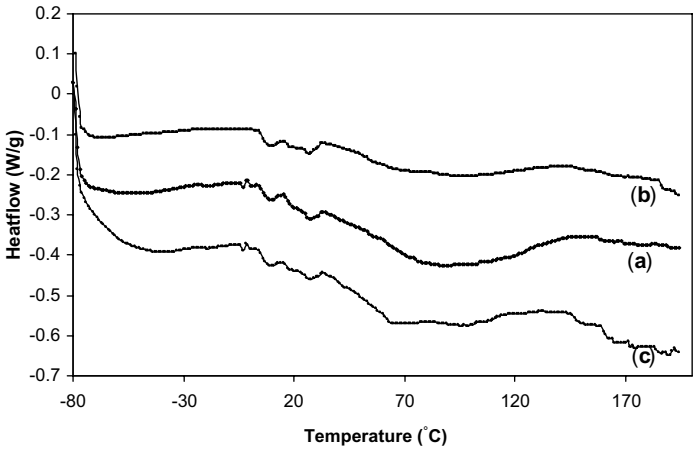


Fig. 8. DSC thermograms of (a) UPR, (b) 5% EPN/UPR, (c) 10% EPN/UPR (heating rate 10 °C/min).

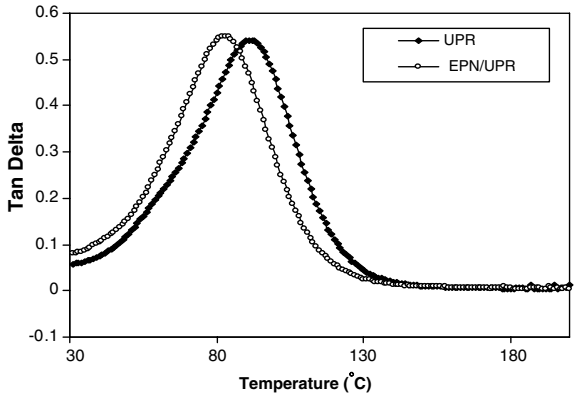


Fig. 9. DMA-tan δ curves (a) UPR, (b) 5% EPN/UPR (heating rate 1 °C/min).

heterogeneity with two T_gs at 61 and 102 °C. Hence, it is concluded that at higher percentages of EPN, part of the EPN remains unattached to the polyester chain.

T_g values obtained from DMA-tan δ curves (Fig. 9) for UPR (92 °C) and UPR/5% EPN (83 °C) are in good agreement with T_g values obtained from DSC curves. The tan δ values at 92 °C for UPR and UPR/5% EPN are 0.5421 and 0.4495, respectively. The marginal lowering may be due to the enhanced crosslinking.

3.5. Morphological studies

Scanning electron micrographs of unmodified and modified UPR fractured at low deformation rate are shown in Fig. 10. 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. The morphology is indicative of brittle fracture. All the fracture surfaces of the blends (b–e) indicate extensive crazing. DGEBA modified resin fracture pattern is shown in micrograph (b). Peak structures and fibrils characteristic of ductile fracture are seen. Referring to EPN modified resin (c), 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 enable one to recognise the stretching that takes place prior to fracture. Extensive stress whitening is also observed. These point to high toughness and load bearing characteristics in the case of (c). The micrograph of ECN modified resin (d) shows crazes which represent the initial stage of ductile force fracture. The fracture paths are branched and less continuous than in the case of the base resin. Micrograph of EPN-1138 modified resin (e) shows a profusion of fracture paths. Greatly increased surface roughness and drawn ridges of polyesters are seen. Branching of fracture paths results in high-energy absorption. From a comparison of the morphologies, the best energy absorbing characteristics are observed for resin (c), a reactive blend of UPR and EPN. The mechanical properties of the blended systems are strongly dependant on the morphology of the dispersed epoxy resins. The epoxy compounds have better miscibility with the polyester and lead to different morphologies. The SEM morphology fractures are in league with the trend in mechanical properties and toughness for various epoxies.

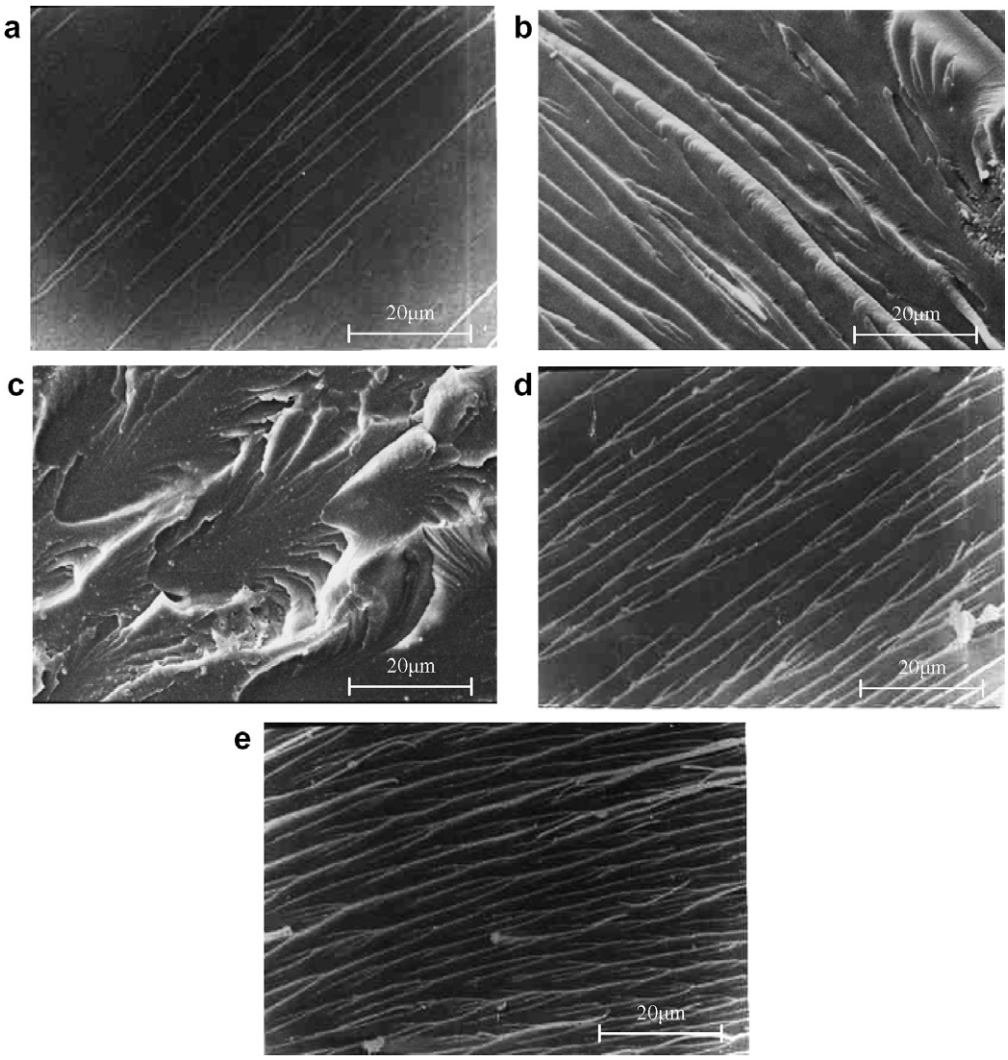


Fig. 10. Scanning electron micrographs of fracture surfaces (a) UPR, (b) DGEBA/UPR, (c) EPN/UPR, (d) ECN/UPR and (e) EPN-1138/UPR.

4. Conclusion

Unlike rubbers, epoxy resins are highly miscible with UPR, thanks to the possibility for co-reaction. EPN is far superior to all other epoxy resins considered in this investigation for blending with UPR. Toughness and tensile properties show maximum improvement at about 5% by wt EPN concentration. The increase in toughness has been achieved with simultaneous increase in tensile strength for all epoxy resin blends. In the case of EPN, 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. EPN/UPR blends show substantial improvement in thermal stability and damping. The morphology of the toughened matrix, as disclosed by SEM, shows clear indications of higher energy absorption and extensive crazing. Epoxy resins in general and EPN in particular can be used as modifiers for UPR at low percentages. The results are of significance to the manufacturers of high quality FRP equipment based on UPR resin. The blends can withstand higher impact loads especially at locations like corners where fibres are few.

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