

Epoxy—Polyester IPNs Modified with Aromatic Amines

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ABSTRACT: Semi-interpenetrating polymer networks (Semi-IPNs) based on epoxy and unsaturated polyester resin (UPR; added in 5.9 and 11.1 wt %) have been prepared by chemical route. Room temperature curing was attempted using triethylene tetramine as a hardener. Blend with 11.1% UPR is found to exhibit best mechanical properties. Further, blends were also prepared by adding aromatic amines such as diphenylamine (DPA, secondary amine) and benzidine (Bz, primary amine). Structural elucidation of the samples through identification of functional groups was carried out with the help of Fourier transform infra red spectroscopy. Absence of peak at 915 cm^{-1} (characteristic of epoxy ring) confirmed complete curing in all the blends. The mechanical properties such as hardness, izod impact and tensile strength of blends were compared. The co-cured blends show decrease in shore hardness ($\approx 1\text{--}6\%$), while, the izod impact exhibits an opposite trend. Blends with

10% DPA and Bz show an increase in izod impact by 268.6% and 38.8% respectively. Further, the tensile strength is observed to be enhanced by 45% in case of DPA while addition of Bz reduces it by 32.8%. Thermal properties were studied by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. TGA shows no significant change in onset and decomposition temperature but temperature at which it melts is lowered almost by $100\text{--}150^\circ\text{C}$ together with the onset temperature (by $\approx 200^\circ\text{C}$) observed in DSC. Scanning electron micrographs reveal granular nature of the samples. The homogeneity of blends appears to be good. The blends co-cured with DPA are relatively crystalline compared with others. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 836–843, 2012

Key words: blends; brittle; cross-linking; differential scanning calorimetry; FT-IR

INTRODUCTION

Epoxy resins are useful as adhesives and as matrix material in advanced composites. However, unmodified (neat) epoxies are brittle and their low fracture energies restrict their use. Numerous chemical modifications on epoxy resins have been reported, especially, interpenetrating polymer networks (IPNs) prepared by blending two thermosets have been extensively used. It proves to be a promising way to extend the range of properties of the thermosets and hence the applications of the polymer products. Several studies on IPNs have revealed enhanced mechanical properties.¹ Epoxy/acrylate IPNs are reported to exhibit improvement in elongation at break, toughness, modulus, and tensile strength.^{2–4} Epoxy/polydimethylsiloxane IPNs show potential toughening,⁵ improved impact, and thermal strength.⁶ Epoxy/poly vinyl acetate IPNs are known for toughness.⁷ Similarly, IPNs of Polyurethane–polystyrene, polyacrylates, and polybenzoxazine, polymethacrylate, and ep-

oxy-amine network are observed to have higher tensile strength and elongation at break, improved thermal and surface free energy, and exhibit gas barrier properties.^{8–10}

Mechanical properties of epoxy/polyethersulfone IPNs are improved on addition of bismaleimide,¹¹ similarly, processability along with T_g , modulus, and fracture energy is higher in case of bisphenol-A-based bismaleimide resin modified by allyl functionalized polyimide,¹² so also are the thermal and mechanical properties of siliconized epoxy modified with bismaleimide.^{13–15} The polyester toughened epoxy systems are also further modified by bismaleimide to alter thermo-mechanical properties.¹⁶

In this work, semi-interpenetrating polymer network (semi-IPN) blends of epoxy (E) and unsaturated polyester resin (UPR) were prepared using triethylene tetramine (TETA) as a room temperature curing agent. UPR are widely used because of their low manufacturing cost, easy processing, and low densities. Epoxy shows good miscibility and compatibility with UPR on blending and co-cured resin shows substantial improvement in toughness and impact resistance.

The semi-IPNs were further modified by adding aromatic amines such as DPA (secondary amine) and Bz (primary amine) to investigate whether they

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TABLE I
Resin/Blend Name and Composition

Resin/blend	Blend composition
E	E
BA	E + UPR (11.1%)
BB	E + UPR (11.1%) + DPA10%
BC	E + UPR (11.1%) + Bz10%
BD	E + UPR (11.1%) + DPA10% + Bz10%
BE	E + UPR (5.9%) + DPA10% + Bz10%

render conductivity to blends along with other properties such as thermal and mechanical. However, the results showed absence of conductivity.

EXPERIMENTAL

All the chemicals used were of AR grade and used as obtained. The commercially available epoxy resin (diglycidyl ether of bisphenol A, DGEBA, epoxy equivalent 180-205), Debecot 520 F and hardener 758 (TETA) used were from ELANTAS Beck India Ltd. Phthalic anhydride was obtained from LOBA India, maleic anhydride was from CDH India and propylene glycol from Merck India.

The UPR was synthesized in laboratory using maleic anhydride, phthalic anhydride and propylene glycol taken in molar ratio as 0.50 : 0.50 : 1.1 respectively. Fifty percent by resin weight (excluding by product water) of styrene was used for preparing UPR.

The films of epoxy and UPR blends were casted by varying the composition of UPR between 0 and 50%. The castings were prepared by pouring mixtures of E, UPR, and TETA (12–13 phr) in the mold (20 × 2 × 0.3 cm) comprised of two parallel mild steel plates screwed at both the ends. The curing of each resin composition was done at room temperature for 24 h. Special attention was given toward maintaining the same curing schedule for each resin composition. The results indicated that only two compositions (5.9 and 11.1% of UPR) yielded homogenous films while other compositions resulted in highly viscous blends.

E-UPR blends were further modified by adding aromatic amines, Bz, and DPA (10 and 50%). Ten

TABLE II
Soxhlet Extraction Data of E-UPR Blends

Sample	Solvents			
	n-Hexane	Chloroform	Acetone	Methanol
E	99.36	95.48	97.35	99.01
BA	98.19	94.62	95.22	93.05
BB	95.11	94.91	87.28	86.11
BC	97.95	95.22	90.14	90.59
BD	96.07	80.17	86.40	80.32
BE	97.96	92.62	90.59	92.11

percent composition was observed to be optimum with improved properties.

TEST METHODS

Mechanical properties

Hardness was measured using Shore hardness tester (Blue steel India, range 20–90 shore D) as per ASTM D2240. Specimens with 3 mm thickness were used. Hardness was determined at five different positions on the specimen at least 6-mm apart and arithmetic mean was taken.

Tensile strength was measured using programmable universal testing machine (Star testing systems, India) as per ASTM D638 at cross head speed 50 mm min⁻¹, using specimen with dimensions 12.5 mm width, 150-mm length, and 3-mm thickness. Notched izod impact strength of each sample was measured using izod impact tester (Zwick, Germany) as per ASTM D256. Specimens with dimensions 13 mm width, 54 mm length, and 3 mm thickness were used.

Thermal properties

Thermogravimetric analysis (TGA) was carried out using a Shimadzu 51 thermal analyzer at a heating rate of 10°C min⁻¹ in oxygen atmosphere at a flow rate of 50 mL min⁻¹. The TGA was recorded from RT to 1000°C.

Differential scanning calorimetry were performed on Shimadzu 6 model in nitrogen atmosphere at a heating rate of 10°C min⁻¹ in nitrogen atmosphere in a temperature range between RT to 1000°C.

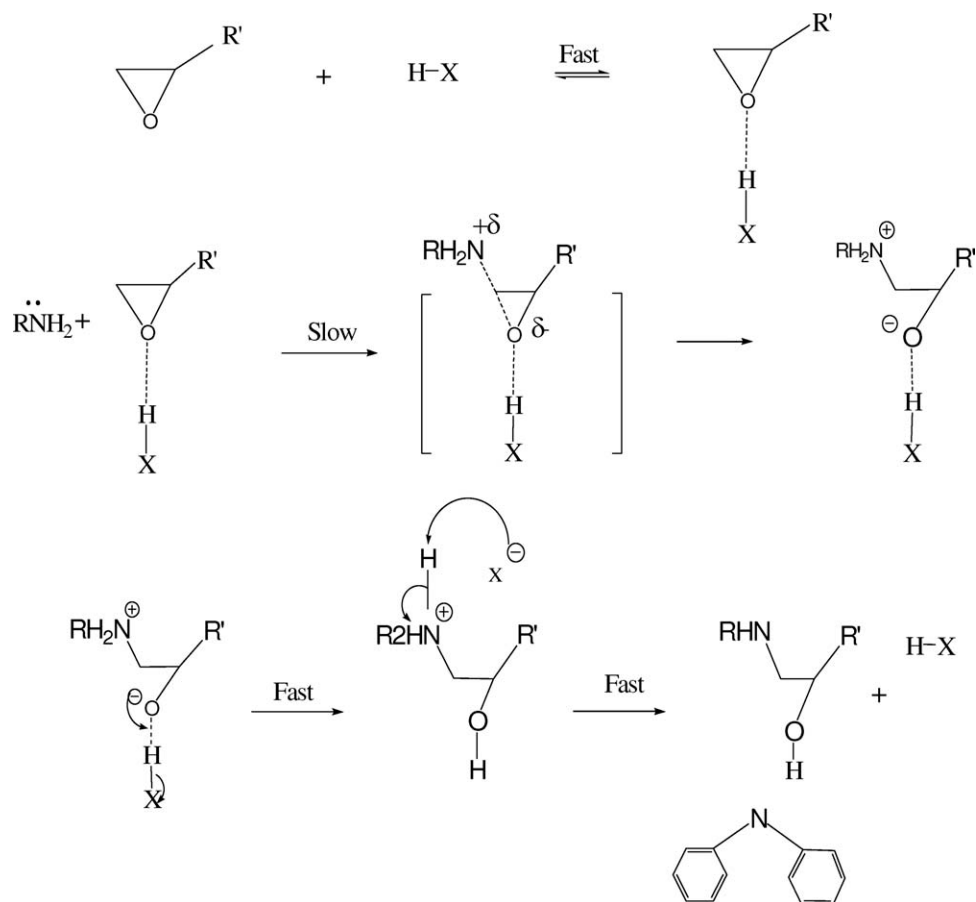
Morphology

The surface morphology of samples were observed with the help of a scanning electron microscope (SEM; JEOL JSM model 630 A). A 0.5 × 0.5 × 0.3 cm sample piece was cut and platinum coating was deposited on all the samples before examination, transverse sections were examined.

TABLE III
Mechanical Properties of E-UPR Blends

Resin/blend	Hardness shore D scale	Izod impact strength (KJ/m)	Tensile strength (MPa)
E	85–86	17.8	33.38
BA	80–81 (–5.9%)	15.60 (–10%)	41.75 (+25%)
BB	82–83 (–3.5%)	64.51 (+268.6%)	48.40 (+45%)
BC	83–84 (–2.4%)	24.29 (+39.8%)	22.41 (–32.8%)
BD	81–82 (–4.7%)	45.80 (+157.3%)	54.86 (+64.4%)
BE	84–85 (–1.2%)	18.38 (+5%)	33.00 (+1.1%)

The data in parenthesis show the percentage of increase or decrease in mechanical properties.



Scheme 1 Ring opening reaction of epoxy catalyzed by H-X.

Fourier transform infra red

FT-IR spectra of the samples were recorded on a Shimadzu 8400 spectrophotometer over a range of 400–4000 cm^{-1} .

Soxhlet extraction

The solvent unextractable matter was determined by the Soxhlet method. Accurately weighed samples were placed in filter paper thimble and then introduced in the siphon cup of Soxhlet and extracted with different solvents (methanol, chloroform, acetone, and n-hexane) near their boiling points till constant weights were obtained.

RESULTS AND DISCUSSION

IPNs of E-UPR were obtained by mixing each of the reactants in appropriate proportions. The cross-linking of E/DGEBA was effected by adding stoichiometric amount of TETA (amine functionality 6) in presence of UPR at room temperature. The affinity of DGEBA to react with TETA is so high that there is negligible possibility of grafting or any reaction between DGEBA and $-\text{OH}$ or $-\text{COOH}$ group of UPR.¹⁷ In presence of a nucleophilic amino group,

the strained epoxy ring opens up preferentially. Moreover, the $-\text{OH}$ group acts as a catalyst only to accelerate cross-linking reaction of epoxy with amine without $-\text{OH}$ group being incorporated into the epoxy resin.¹⁷ Thus, the probability of $-\text{OH}$ of UPR to bond with DGEBA are further reduced.

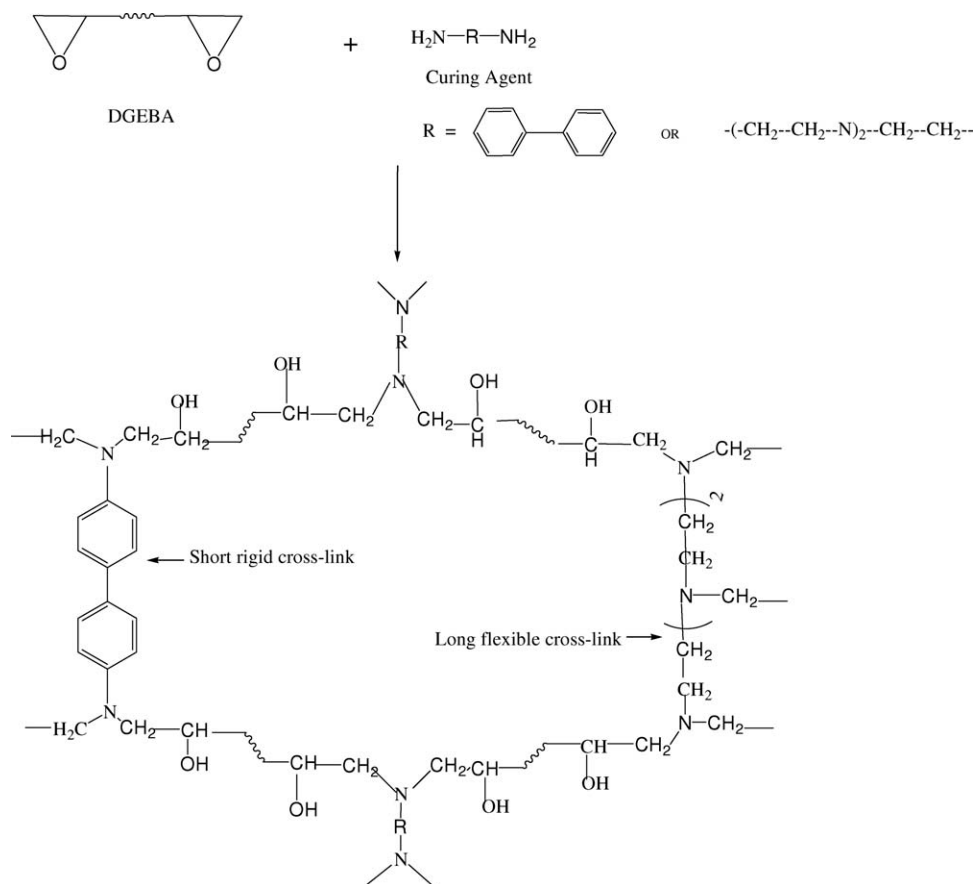
In addition to this, the IPNs were modified by adding amines such as Bz and DPA. The samples thus prepared were analyzed for solvent resistance, mechanical, and thermal properties. The various blend formulations are named as per Table I.

Solvent extraction

The Soxhlet extraction data are given in Table II. From the results, it is observed that the epoxy resin exhibits the highest resistance in each of the solvents. The solvent resistance is seen to decrease in case of blends (samples BA–BE). However, the change is negligible $\sim 3\text{--}4\%$ and maximum 10% except for blend BD extracted with methanol and chloroform, where it is higher.

Mechanical properties

As noted from the Table III, the tensile strength of BA is improved compared with neat epoxy (E) while



Scheme 2 Cross-linked epoxy matrix.

the hardness and impact strength is reduced, this can be attributed to the plastic nature induced by UPR in the IPN. Further, the tensile strength is observed to improve in case of blend BB by $\sim 45\%$ together with the impact strength increasing by $\sim 270\%$ while the hardness shows a slight decrease. These results can be accounted in terms of amine functionality of DPA which is 1, when blended with epoxy, the electron withdrawing benzene rings of DPA would diminish the nucleophilicity of amino group, hence the hydrogen atom on the amine group would be electron deficient and act as a donor molecule (H-X). Epoxide forms hydrogen bond with donor molecule. In hydrogen bonded epoxide, the H-X and C-O bonds are somewhat weakened. The nucleophilic primary amine reacts more readily with hydrogen bonded epoxide, i.e., the ring opening reaction is catalyzed by H-X,¹⁸ thereby accelerating the cross-linking reaction. A termolecular transition state is expected in such H-bond donor assisted nucleophilic attack of amino group on epoxy ring of DGEBA, this can be explained by the reaction Scheme 1. After complete curing of epoxy by TETA, the DPA must be held in the matrix through H-bonding of OH groups of E-UPR.

The blend BC with Bz (amine functionality 4), blended along with TETA (amine functionality 6),

Bz being primary amine probably competes with TETA in opening of epoxy ring and participates in cross-linking. The cured structure may consist of a mixture of short and long chain cross-links, the Bz cross-links being short and rigid, prevent chain movement and chain flexibility resulting in decrease in the tensile strength ($\sim 32.8\%$), while the TETA cross-links are expected to be longer and flexible.¹⁹ The benzene rings would further increase the free volume in cross-linked matrix, resulting in izod impact enhanced by 38.8%. The cross-linked epoxy matrix with Bz and TETA is shown in Scheme 2.

The overall decrease in hardness observed in blends compared with neat epoxy casting may be due to higher degree of flexibility/and higher degree of free volume in the matrix.

Thermal properties

The TGA of sample E and blends were performed in the temperature range between RT to 1000°C in oxygen atmosphere. From the results of TG analysis, the blends are observed to exhibit slightly lower thermal stability in comparison with pure epoxy resin. Three step decomposition pattern is observed with the final decomposition temperature being around 600°C. Table IV shows the weight losses and

TABLE IV
TG Results of E-UPR Blends

Sample	ΔT (°C)	Δm %	ΔT (°C)	Δm %	ΔT (°C)	Δm %
E	152–371	3.6	371–480.9	62.2	500–542.7	34.2
BA	120–352.3	9.1	352.3–452	62.3	504.7–523.8	28.2
BB	120–352.3	19.1	352.3–476	55.8	514–561.9	23.4
BC	123–371.4	13.5	371–490	54.1	504.7–547.6	31.5
BD	128–361.9	13.5	361.1–447	54.1	504.7–552	32.4

the respective temperatures as noted from the thermograms, (ΔT) represents interval of temperature where mass loss (Δm) was observed. The weight loss in the first step varies between 3 and 19%. In case of neat epoxy, the loss arises due to the unreacted monomer molecules trapped in the matrix while in IPNs it can be attributed to the loss of styrene (used as diluent for UPR) and DPA which does not participate in chemical bonding in IPN. The second step weight loss (54–62%) could be associated with the degradation of TETA cross-links and aliphatic constituents along with UPR. The rapid weight loss (23–34%) in the third step involves the degradation process of aromatic components including Bz cross-links. The percentage loss is consistent with loss predicted from the structure of various blends and weight percentage of all components of the blends. Figure 1 shows the differential scanning calorimetric (DSC) plots of the samples exhibiting peaks corresponding to the decomposition of various fragments as seen in thermograms. Comparison of the onset temperatures and energies of decomposition of the polymer backbone reveals the epoxy to be the strongest matrix with highest decomposition energy followed by the blends BA, BB, BC, and others. These results are in agreement with the mechanical properties observed for neat epoxy and blends.

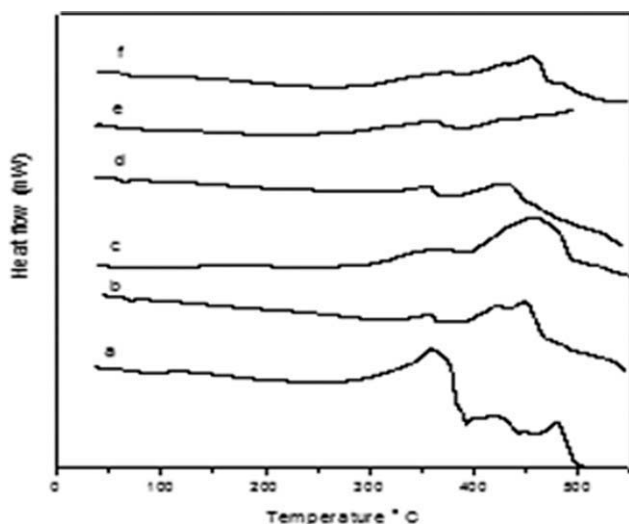


Figure 1 DSC curves of (a) resin E, (b) blend BA, (c) blend BB, (d) blend BC, (e) blend BD and (f) blend BE.

TABLE V
DSC Data for E-UPR Blends

Sample	Onset temperature (°C)	Heat (J/g)	Height (mW)
E	563.69	–10.54	–8.26
BA	362.15	–131.59	–4.29
BB	371.97	–197.42	–4.99
BC	362.71	–107.35	–4.26
BD	368.01	–61.08	–3.17
BE	376.42	–65.27	–1.74

Table V gives the data obtained from the DSC analysis of the samples.

Spectral studies

Figure 2 shows the overlaps of the FT-IR spectra of the samples and the characteristic frequencies observed for various stretching and bending vibrations are given in Table VI.²⁰ The C–O stretching vibrations of the epoxide ring in neat epoxy appear at 916 cm^{-1} . In case of blends, the absence of this peak indicates the epoxide ring opening, i.e., complete curing of the epoxy. The C–OH frequency observed in neat epoxy is at 3475 cm^{-1} which shows a shift toward lower frequencies in case of blends due to hydrogen bonding. Blends with DPA (blends BB, BD, and BE) show intense N–H wagging band at 750 cm^{-1} implying that it does not participate in bond formation.

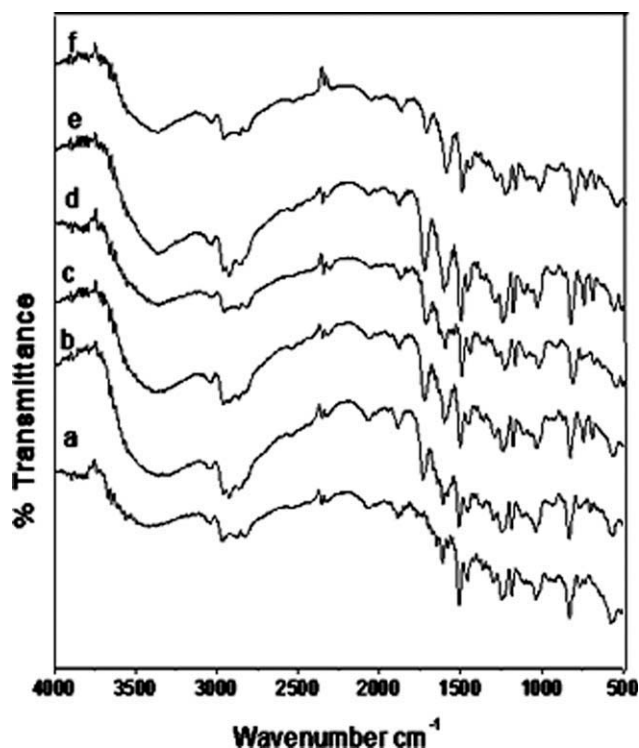


Figure 2 FT-IR spectra of (a) resin E, (b) blend BA, (c) blend BB, (d) blend BC, (e) blend BD, and (f) blend BE.

TABLE VI
IR Absorption Bands of E-UPR Blends

IR (frequency, cm^{-1})	E	BA	BB	BC	BD	BE
C—OH Str	3475	3362	3408	3371	3369	3369
—CH ₂ —, —CH ₃ assym Str	2964	2960	2962, 2924	2964, 2928	2924	2964
—CH ₂ —, —CH ₃ sym Str	2860	2868	2837	2825	2850	2827
Ar—CH overtones	2000–1800	2000–1800	2000–1800	2000–1800	2000–1800	2000–1800
C=O Str	—	1730	1728	1730	1726	1730
ArC=C—H Str	1608, 1508	1604, 1508	1604, 1508	1610, 1508	1606, 1508	1604, 1508
—CH ₂ —, —CH ₃ bending	1456	1460	1454	1467	1465	1467
C—N Str	1296	1294	1294	1292	1292	1292
—C—C—O—C Str	1246, 1182	1246, 1182	1246, 1182	1246, 1182	1246, 1182	1246, 1182
C—O—C Str	1035	1035	1035	1035	1035	1035
Ar =C—H, C—H & Ar 1,4,substituted ring	829, 731	829, 698	829, 694	829, 698	829, 694	829, 694
N—H Wagging (secondary amine)	—	—	750	—	750	750
—C—H, —N—H bend	572, 513	563	557	561, 648	559, 503	569, 559

Morphological studies

Scanning electron micrographs of sample E and blends before and after izod impact test are shown in Figures 3–5. The neat epoxy appears to exhibit granular structure (crystalline phase) with stressed regions appearing as white patches. After impact, random cracks are seen to propagate in the matrix reducing the grain size with voids or cavitation in the matrix that can be attributed to brittle nature of neat epoxy. Micrograph of blend BA shows smoother structure with strained regions, the fractured surface shows crack propagation after screwing/twisting of surface with stress whitening at the boundaries.

The blend BB exhibits structure intermediate between neat epoxy and blend BA, the structure is relatively smooth with stress free regions before fracture. After fracture, parabolic cracks appear in the matrix. The fracture path shows a feathery texture, the wavy crest enables one to recognize the strengthening that takes place before fracture. In case of blend BC, the enhanced degree of stressed regions with larger sized granules is observed. After impact, deeper cracks with cavitation can be noted. The micrograph of blend BD also depicts smoother morphology with finer size granules and show homogeneity in the matrix. After fracture, extended wavy cracks can be visualized together with stress whitening. On the other hand, blend BE exhibits,

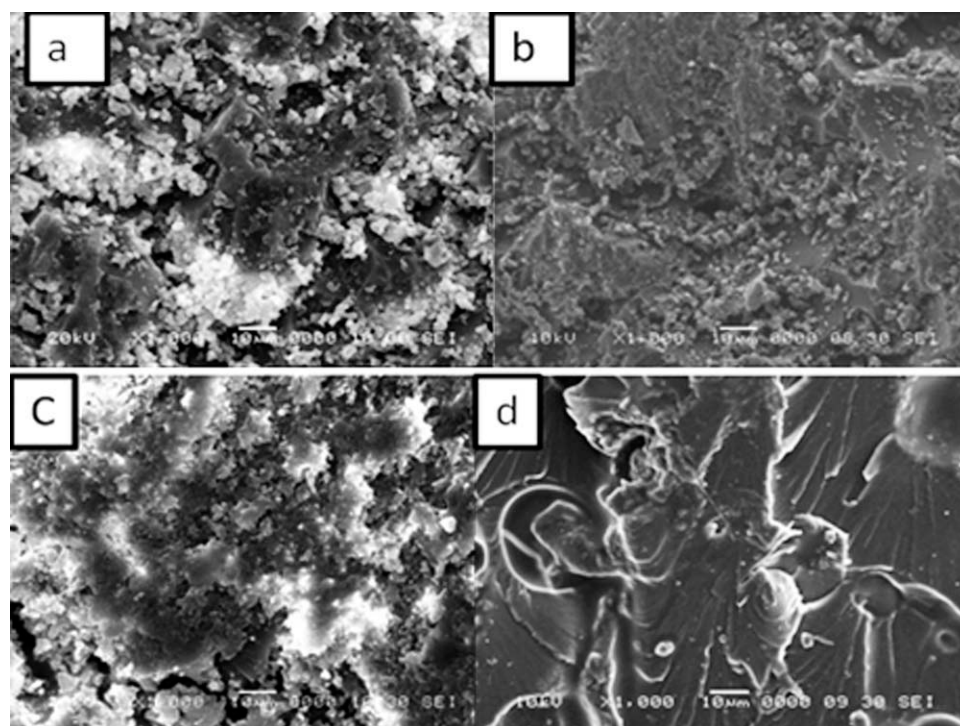


Figure 3 Micrographs of resin E (a) before impact, (b) after impact and blend BA (c) before impact, (d) after impact.

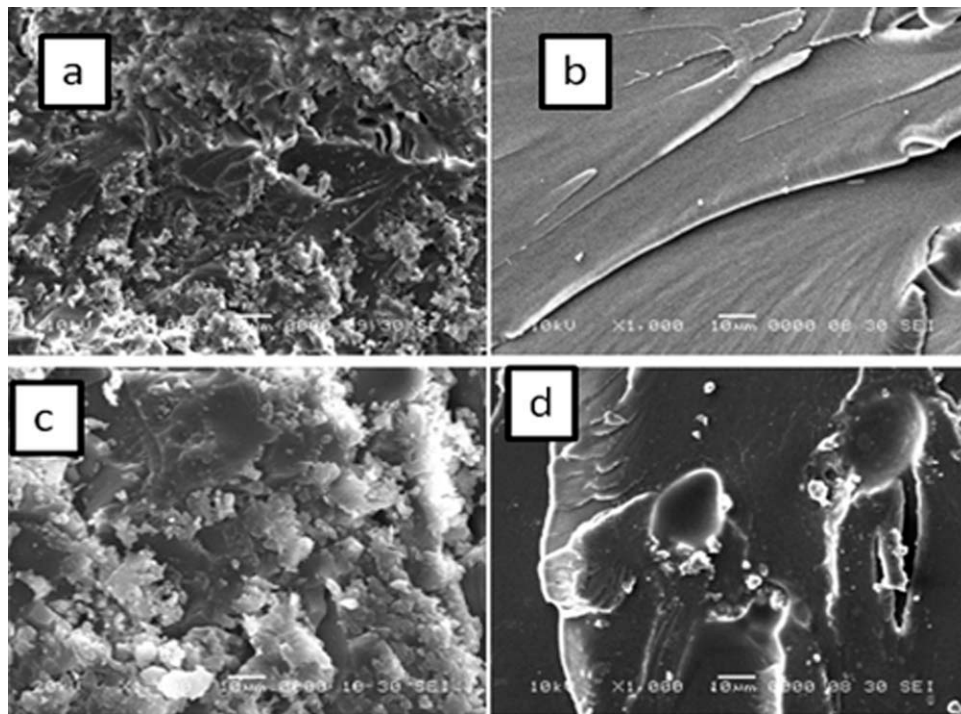


Figure 4 Micrographs of blend BB (a) before impact, (b) after impact and blend BC (c) before impact, (d) after impact.

distinct regions of strain in unfractured sample, while the morphology after fracture show severe damage with deeply propagated cracks as the matrix is brittle compared with sample BA.

Compared with neat epoxy, fragility of blend BA seems to decrease due to plastic nature of UPR. Blend BB shows enhanced flexibility, whereas blend BC due to rigid structure of Bz adds to fragile

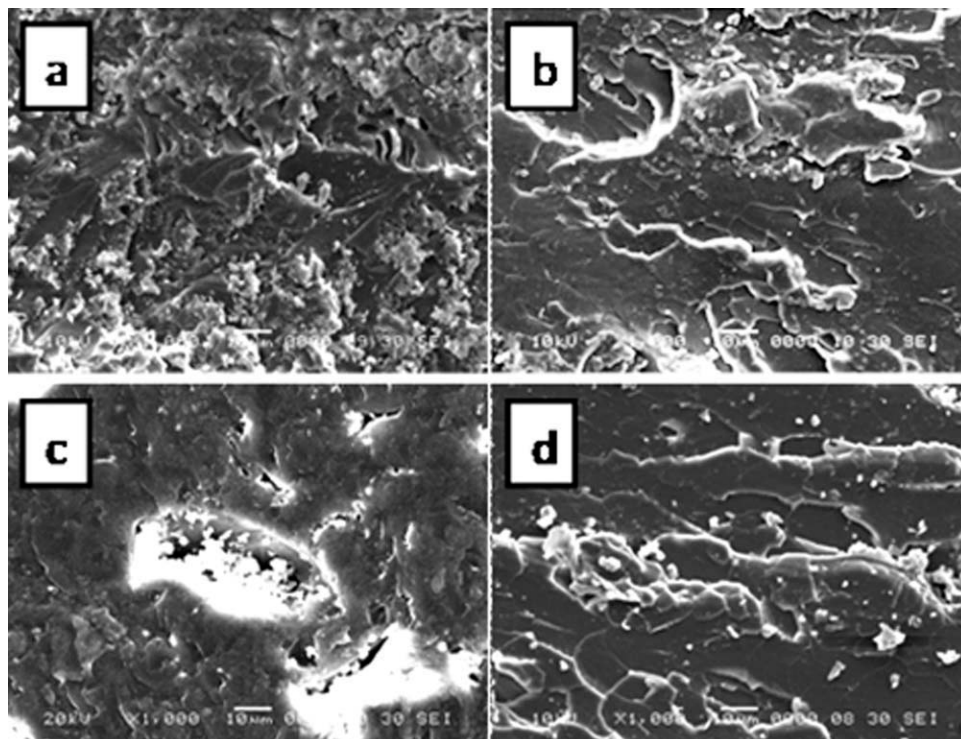


Figure 5 Micrographs of blend BD (a) before impact, (b) after impact and blend BE (c) before impact, (d) after impact.

nature. The mixed blends exhibit intermediate behavior. The morphological results are in good agreement with the trend observed in mechanical properties of blends.

CONCLUSION

E-UPR IPN blends exhibit improved mechanical properties compared with neat epoxy. The modified blend BB is observed to have best mechanical properties, without seriously affecting thermal properties. However, the solvent resistance of blends is slightly lower than neat epoxy. SEM shows granular nature and the homogeneity of blends appears to be good.

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References

1. Rosu, L.; Cascava, C. N.; Ciobanu, D.; Rosu, D.; Ion, D. E.; Morosanu, C.; Enachesku, M. *J Photochem Photobiol A: Chem* 2005, 169, 177.
2. Das, B.; Chakraborty, D.; Hajra, A. *Eur Polym J* 1994, 30, 1269.
3. Chakraborty, D. *Polym Gels Networks* 1998, 6, 191.
4. Das, B.; Chakraborty, D. *Polym Gels Networks* 1995, 3, 197.
5. Hanoosh, W. S.; Abdelrazaq, E. M. *Malaysian Polym J* 2009, 4, 52.
6. Thanikai, T. V.; Bilal, M. I. *Bull Mater Sci* 2000, 23, 425.
7. Lapprand, A.; Arribas, C.; Salom, C.; Masegosa, R.; Prolongo, M. *J Mater Process Tech* 2003, 143, 827.
8. Chu-Hua, L.; Yi-Che, S.; Chih-Feng, W.; Chih-Feng, H.; Yuung-Ching, S.; Feng-Chih, C. *Polymer* 2008, 49, 4852.
9. Hui, C.; Jiann-Ming, C. *J Appl Polym Sci* 1993, 50, 495.
10. Simic, V.; Boileau, S.; Bouteiller, L.; Gallez, L.; Merlin, P. *Eur Polym J* 2002, 38, 2449.
11. Rajasekaran, R.; Alagar, M.; Karikal Chozhan, C. *Exp Polym Lett* 2008, 2, 339.
12. Qin, H.; Mather, P.; Baek, J.; Tan, L. *Polymer* 2006, 47, 2813.
13. Ashok Kumar, A.; Alagar, M.; Rao, R. M. V. G. K. *J Appl Polym Sci* 2001, 81, 38.
14. Ashok Kumar, A.; Alagar, M.; Rao, R. M. V. G. K. *J Appl Polym Sci* 2001, 81, 2330.
15. Suresh Kumar, R.; Alagar, M. *J Appl Polym Sci* 2006, 101, 668.
16. Dinakaran, K.; Alagar, M. *J Appl Polym Sci* 2002, 85, 2853.
17. Mukherjee, G.; Saraf, M. *J Polym Sci: Part B: Polym Phys* 1995, 33, 855.
18. Smith, I. T. *Polymer* 1961, 2, 95.
19. Breach, C. D.; Folks, M. J.; Barton, J. M. *Polymer* 1992, 33, 3080.
20. Nikolic, G.; Zlatkovic, S.; Cakic, M.; Cacki, S.; Lacnjevac, C.; Rajic, Z. *Sensors* 2010, 10, 684.