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Studies on the blends of modified epoxy resin and carboxyl-terminated polybutadiene (CTPB)—II: thermal and mechanical characteristics

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Abstract Blend samples were prepared by physical mixing of resole–epoxy blend with carboxyl-terminated polybutadiene (CTPB) liquid rubber ranging between 0 and 25 wt% in the interval of 5 wt%. Resoles were synthesized with phenol and various alkyl phenols. The blends were cured with 40 wt% polyamide. The structural changes during the curing were investigated by infra-red spectroscopic analysis. The presence of CTPB in resole-epoxy blends did not affected the values of cure times and ΔH whereas the gel time decreased up to 15 wt% addition of CTPB in the blends. The blend systems containing *p*-cresolic resole, epoxy and CTPB showed minimum gel time amongst all other blend samples. A clear-cut two-step mass loss in thermogravimetric (TG) trace of unmodified and CTPB-modified systems was observed. The mechanical properties of the blend samples were found to be affected by the CTPB addition. The plane strain fracture toughness (K_{IC}) values of CTPB-modified matrix resins were greater that that for the unmodified resole/epoxy blends. This was further verified by scanning electron microscopic (SEM) analysis.

Introduction

Cured epoxy resins (ERs) are known to exhibit good engineering properties such as high stiffness and strength, creep resistance, chemical resistance and good adhesion to many substrates [1], etc., and are extensively employed in several important applications such as structural adhesives, surface coatings, advanced composites for the aerospace, electronic industries, etc. However, they are inherently brittle in the cured state. To alleviate this deficiency, epoxy resins are frequently modified by dissolving in a small amount (10–20%) of reactive liquid rubber. This can greatly improve the fracture toughness of the ERs by the precipitation of cross-linked rubbery particles during curing [2–4]. The use of low-molecular weight rubber is recommended to ensure that the viscosity of the resin is not increased excessively so that processability of the system is not impaired [5].

Most of the work reported in the field of toughened epoxies deal with diglycidyl ether of bisphenol A (DGEBA) based epoxy resin and liquid carboxyl-terminated butadiene acrylonitrile (CTBN) copolymer [6–12]. Modification of epoxidised novolac and resole with CTBN has been studied to a lesser extent [13–15]. Novolac epoxy resins, being multifunctional , can produce a more tightly crosslinked three-dimensional network compared to DGEBA.

Carboxyl-terminated polybutadiene (CTPB) liquid rubber, mainly used in composite rocket propellants as a binder [16], has also been used as rubber-toughened by very few researchers [17, 18]. Nigam et al. [17] investigated the toughening of epoxy-novolac resin with the addition of CTPB. They found that the addition of 10 wt% CTPB into the epoxy matrix gave the optimum mechanical properties. We have also prepared coating compositions from epoxidised resole and CTPB [18] and studied the effect of various chemicals on the surface of the cured films of the blend

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compositions. Furthermore, we have from the blends of resole, epoxy and CTPB and studied their mechanical and thermal properties along with morphological changes of the blends, in the present investigation.

Experimental

Materials

Formaldehyde, phenol, *o*-, *p*-, *m*-cresols and sodium hydroxide, all LR grades, of M/s Thomas Baker Chemicals Ltd., Mumbai were used for the preparation of various resoles. The glycidyl ether of bisphenol-A (DGEBA)-based epoxy, used in all experiments, was R-100 with a number-average molecular weight (M_n) of 380 and an epoxide equivalent of 192 g/equiv. as determined by acid titration [19]. The curing agent was PH-851 with amine value of 240–400 mg KOH/g. Both the epoxy and curing agent were procured from M/s Resinova Pvt. Ltd., Kanpur, India. Carboxyl-terminated Polybutadiene (CTPB) liquid rubber (Hycar 2000 × 162) was kindly supplied as free sample by M/s Emerald Performance Materials, LLC, Hong Kong.

Synthesis of resoles

Resoles, from various alkyl phenols, viz., *o*-, *p*-, and *m*-cresoles, separately with formaldehyde (37% v/v), were synthesized as per the procedure similar to given in our previous publication [18] for the synthesis of phenol and formaldehyde. The contents were reacted in a three-necked R. B. flask in excess of water at 70 °C for 2–3 h. The pH and free-formaldehyde content were checked after every 15 min throughout the reaction. Two layers were formed, if stirring was stopped. About 10% sulfuric acid was added to bring down the pH in between 6 and 7. The water and methanol, present in the reaction medium after the completion of the reaction, were removed by vacuum distillation under reduced pressure (30–35 mm of Hg). The prepared samples were analysed with infra-red spectroscopic analysis.

Preparation and curing of blends

The resoles synthesized in section 2.2 were, separately, blended with DGEBA-epoxy resin in equal weight ratios. Each blend samples were, further, mixed for 60 min with varied concentrations of CTPB as per the formulations given in Table 1 at temperatures well below the cure temperatures of the respective resoles. After mixing, the mixture was degassed in a vacuum chamber for 5 min. Polyamide (40 wt% based on the total amount of the blend) was then added to the mixture was now heated and stirred for 15–20 min (at temperatures well below the cure temperatures of respective resoles) until complete dissolution of the polyamide. The mixture was further degassed in a vacuum chamber for 2–3 min and poured into appropriated open molds for mechanical testings. The curing of blend samples was performed in an air oven (M/s Indian Equipment Corporation, Mumbai, India) at 100 °C for different time periods.

Table 1 Blend composition details and DSC data

S. No.	Resole/Epoxy blend in equal weight ratio	CTPB (wt%)	Sample Code	ΔH (J/g)	Gel Time (s)	Cure time at 100°C (min)
1.	ER_1	0	EC_0R_1	149.5	120	60
		5	EC_5R_1	128.4	101	54
		10	$EC_{10}R_1$	127.1	92	46
		15	$EC_{15}R_1$	126.4	86	40
		20	$EC_{20}R_1$	127.3	98	44
		25	$EC_{25}R_1$	127.9	106	50
2.	ER_2	0	EC_0R_2	125.8	102	56
		5	EC_5R_2	104.2	93	50
		10	$EC_{10}R_2$	104.4	84	43
		15	$EC_{15}R_2$	102.5	72	38
		20	$EC_{20}R_2$	103.1	87	43
		25	$EC_{25}R_2$	103.7	99	48
3.	ER_3	0	EC_0R_3	112.6	96	46
		5	EC_5R_3	98.1	82	32
		10	$EC_{10}R_3$	97.2	78	30
		15	$EC_{15}R_3$	96.1	66	25
		20	$EC_{20}R_3$	97.3	70	29
		25	$EC_{25}R_3$	97.9	79	36
4.	ER_4	0	EC_0R_4	138.9	111	50
		5	EC_5R_4	109.7	98	36
		10	$EC_{10}R_4$	108.1	83	31
		15	$EC_{15}R_4$	107.3	75	28
		20	$EC_{20}R_4$	107.8	89	34
		25	$EC_{25}R_4$	108.4	104	39

R_1—Resole from phenol; R_2—Resole from *o*-cresol; R_3—Resole from *p*-cresol; R_4—Resole from *m*-cresol; E—Epoxy

Characterization

Fourier-transform infrared (FTIR) analysis was performed on a Bruker Victor (Model 2.2) spectrophotometer in the wavelength range of 200–4000 cm^{-1}. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC-2910 equipment. The cure conditions were determined in dynamic mode at 10 °C/min under nitrogen atmosphere and this has been employed to complete the curing process in an air oven.

The gel point was determined according to ASTM-2471, by putting about 100 mg of the sample in several tubes, which were placed in an oil bath at 100 °C. The tubes were withdrawn from the bath at different times and chilled in an ice-bath to quench the reaction. The polymeric material was dissolved with tetrahydrofuran (THF). The gelation point was determined from the presence of insoluble fraction.

Thermogravimetric analysis (TGA) was carried out using Du-Pont (Model 2100) TGA, at a heating rate of 10 °C/min in nitrogen atmosphere with flow rate 10^4 mm^3/min from ambient to 800 °C. On comparing the initial degradation temperatures (IDTs) at 5% weight loss of different samples gave the relative thermal stability of the blend samples.

The scanning electron micrograph (SEM) was performed by using a JEOL JSM-35 CF SEM to analyze the morphology of the blends. The cast sheet samples were fractured under liquid nitrogen to avoid any deformation of the rubber capsules inside the epoxy matrix. The fractured surfaces were then sputter coated with gold without touching the surface. Subsequently, the gold coated samples were studied under the SEM for morphological information.

Mechanical testing

The tensile tests were performed using Universal Testing Machine (UTM)(STAR TESTING SYSTEMS, Mumbai, India) at a crosshead speed of 5 mm/min according to ASTM D638. All testings were conducted at ambient conditions of 25 °C and 50% humidity (RH) in an environmentally controlled room. The values were taken from an average of at least five specimens.

Flexural tests were performed by the same UTM fitted with a three-point binding fixture at a crosshead speed of 5 mm/min, according to ASTM D-790. The dimensions of the specimens were 75 × 25 × 2 mm and the span-to-thickness ratio was set at L/D = 32 to 1 in all cases. The values were taken from an average of at least five specimens.

The impact strength of the notched specimens was determined by using a Tinuis Olsen computer controlled (Model 8000 A) UTM having a hammer mass which was deflected at 90° angle from the vertical and allowed to fall and strike the samples. The rectangular specimens of 75 × 12 × 4 mm were taken according to ASTM D-256. The tests were carried out at room temperature and the values were taken from an average of at least five specimens.

Six-millimeter thick samples were used for specimens to determine fracture toughness (Fig. 1).

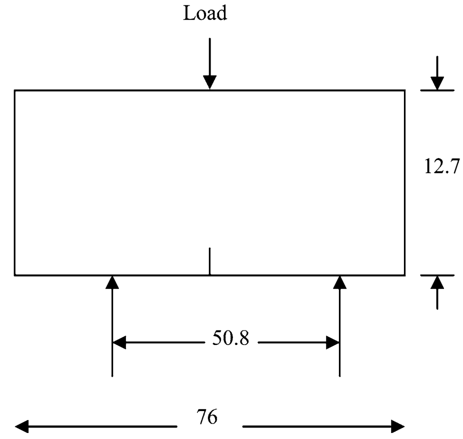


Fig. 1 Schematic illustration of the SEN-3PB specimen used in this study. Dimension are in millimeters

It employed precracked, single-edge notched (SEN) specimens loaded in three-point bending geometry. The ASTM D5045 guidelines were followed to measure the plane strain fracture toughness (K_{IC}). Pre-cracks were introduced to the notched bars by hammering a razor blade which was chilled in liquid nitrogen. These tests were performed over UTM at a crosshead speed of 5 mm/min. K_{IC} values reported represent averages of a minimum of five tests. The following equations were used to calculate K_{IC} which was in accordance to reference [20].

$$K_{IC} = \frac{10^{3/2} \times P \times S}{t \times w^{3/2}} f(x) \tag{1}$$

$$f(x) = 3x^{1/2} \frac{1.99 - x(1-x)\left(2.15 - 3.93 + 2.7x^2\right)}{2(1+2x)(1-x)^{3/2}} \tag{2}$$

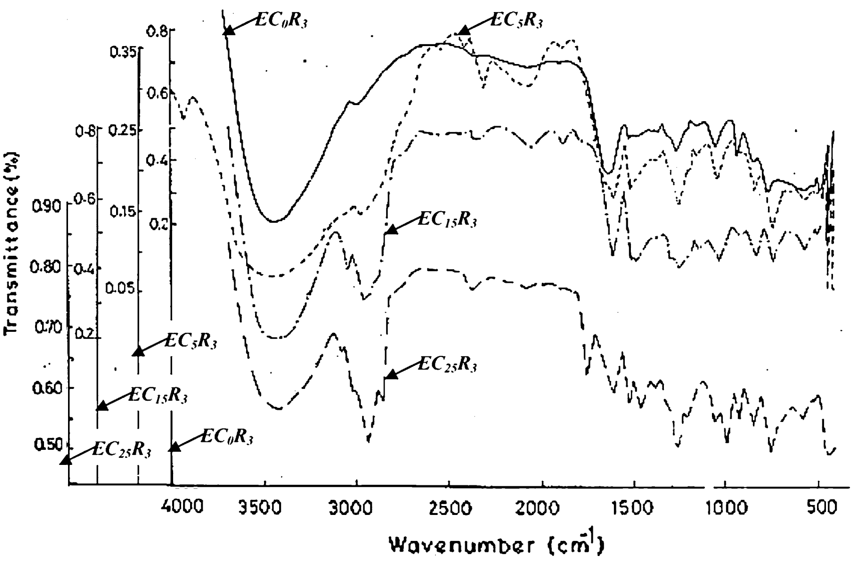
where P is the critical load for crack propagation (kN), S the span length (mm), t the specimen thickness (mm), w the specimen width (mm), f(x) the non-dimensional shape factor, x the crack length to specimen width ratio, a/w, a the crack length measured after the specimen breaks (mm).

Results and discussion

Characterization of resole/epoxy/CTPB blends by FTIR

Figure 2 presents the FTIR spectra of resole / epoxy blend with and without CTPB having polyamide as curing agent. FTIR spectra of uncured blend sample (sample EC_0R_3) showed the characteristics peaks at

Fig. 2 FTIR-spectra of uncured and cured samples of *p*-cresolic resole, epoxy and 15 wt% CTPB



860 and 910 cm^{-1} due to oxirane ring functionality of the epoxy, at 1620 cm^{-1} (N–H bending) and 1650 cm^{-1} (carbonyl stretching) of polyamide and a broad peak near 3400–3500 cm^{-1} due to –OH stretching of aromatic hydroxyl group of the resole. Formation of stretched peak in the region of 850–950 cm^{-1} and at 850–1050 cm^{-1} were observed which might be attributed to O–H bending and C–O stretching vibrations as well as consumption of epoxy groups. Esterification between oxirane group and carboxyl groups might be attributed due to appearance of carboxylate anion at 1550–1610 cm^{-1} and 1300–1400 cm^{-1}. The disappearance of peaks at 1700–1730 cm^{-1} confirmed the reaction of carboxyl group and epoxide group. Also, the peak disappeared near 3400–3500 cm^{-1} confirmed the consumption of aromatic hydroxyl groups as the curing commenced.

Evaluation of cure parameters

The effect of CTPB addition on various cure parameters, viz., cure time at 100 °C, the values of ΔH, and gel time, of different blend samples has been presented in Table 1. It is evident from the table that both cure time and ΔH values are not appreciable affected by the presence of CTPB. However, the cure time decreased up to 15 wt% CTPB addition in the blends and increased thereafter. This might be attributed that the addition of CTPB in resole/epoxy matrix might accelerate the rate of curing reactions. Also, up to 15 wt% addition, a small amount of carboxyl groups in the rubber phase (which was not detected by titration) might be present, which might influence the curing process. Beyond 15 wt% CTPB addition, most of the carboxyl groups from CTPB might be consumed and the curing would proceed only with polyamide, which increased the cure time. It is also clear from Table 1 that the blend samples containing *p*-cresolic resole, epoxy and 15 wt% CTPB showed the least cure time amongst all other blend samples. This could probably due to higher reactivity of the resole/epoxy matrix towards carboxyl groups of CTPB in presence of polyamide.

The ΔH values related to the cure process were determined (Table 1) from the area of the exotherm peak obtained from DSC analysis, taken in the dynamic mode (Fig. 3). This peak appeared during the first heating run but was completely absent during the second heating cycle. The presence of CTPB did not affect significantly the ΔH values, indicating no influence on the crosslink degree of the resole/epoxy resins.

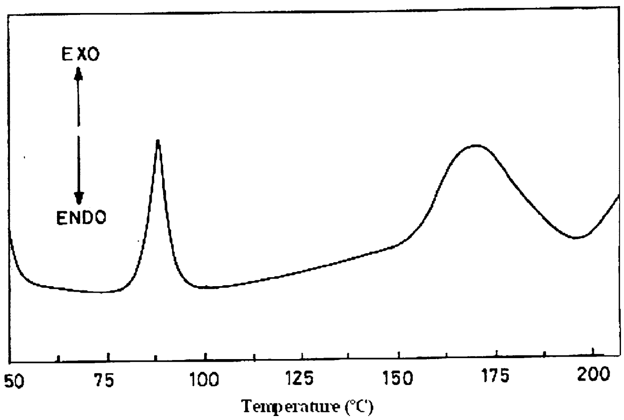


Fig. 3 DSC scan of blend sample of *p*-cresolic resole, epoxy and 15 wt% CTPB

The necessary time to produce the minimum amount of insoluble material (gel time) decreased when resole/epoxy matrix was modified by CTPB. It was also observed that the gel time decreased up to 15 wt% addition of CTPB in the resole/epoxy matrix and then increased. This might be attributed that the addition of CTPB in the matrix might accelerate the formation of the insoluble material. Also, up to 15 wt% addition, a small amount of carboxyl groups in the rubber phase, not detected by titration, might be present which influenced the curing process. These results were quite different from those reported in the literature for epoxy systems modified with CTBN [8] or carboxyl-terminated acrylate rubber [11] and quite similar to those reported by Barcia et al. [21] for epoxy systems modified with epoxide end-capped HTPB rubber. Further, it is evident from Table 1 that the blend systems containing *p*-cresolic resole, epoxy and CTPB showed minimum gel time amongst all other blend systems.

Thermal stability

The blend systems were evaluated for thermal stability in nitrogen atmosphere by thermogravimetric analysis. The thermogravimetric (TG) as well as the differential thermogravimetric (DTG) traces obtained for the unmodified, blend sample, EC_0R_3, and the optimum CTPB-modified formulation (i.e. blend sample $EC_{15}R_3$) are shown in Fig. 4. The data on onset temperature of degradation (T_o), temperature of maximum rate of mass loss (T_{max}) and extrapolated final decomposition temperature (T_F) as well as char yield at 800 °C (which compared the relative thermal stability of the cured blend samples), derived from these traces are given in Table 2. The clear-cut two-step mass-loss in TG trace of unmodified and CTPB-modified systems and the shoulders observed in DTG traces of these blend samples indicated a two-step decomposition behaviour (Fig. 4). The degradation of blend samples, EC_5R_3 and EC_5R_4, were in a single-step.

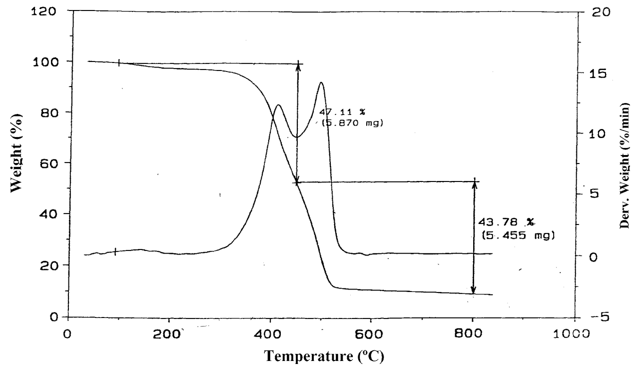


Fig. 4 TG-trace of blend sample of *p*-cresolic resole, epoxy and 15 wt% CTPB

With the initial addition of 5 wt% CTPB in unmodified resole/epoxy blend systems, in the first-step a marginal increase in T_o was seen whereas the addition of CTPB decreased the values of T_o in the second-step (except in blend sample EC_5R_1, where T_o increased). The addition of increased rubber content, i.e., up to 15 wt% in unmodified blends showed the enhancement in the thermal stability of the blends. The variation in the values of char yield with CTPB addition also indicated the same (refer Table 2). When compared to unmodified blend systems, CTPB-modified blend systems had higher char residue at 800°C. This can be attributed to the presence of carboxyl groups in the later, imparting these better thermal stability.

Initially, the degradation behaviour of the cured blend systems remained unaltered as it might be independent of the addition of rubber. With rise in temperature, the rubber might act as thermal stabilizer, and thus increased the thermal stability of the blend systems.

Mechanical properties

The impact strength, flexural and tensile properties, and fracture toughness data of blend samples of resole/epoxy/CTPB containing different amounts of CTPB are summarized in Table 3. It is evident from the data that the tensile strength and modulus values for the blends showed an increasing trend up to 15 wt% of CTPB beyond which a rapid fall was observed. Tensile strength for the rubbery epoxy blends depended on the extent of reinforcement. The increase in the tensile strength might be due to carboxyl content and thereby the possibility of chemical interaction between the constituent molecules of the blend systems. Increased rubber content, e.g., 20 and 25 wt%, resulted in enlarged particles and cavitations in the resole/epoxy matrix, which might cause a net decrease of the total surface area available the rubber particle to establish rubber-matrix adhesion. Thus, heterogeneity of the blends in the molecular scale at higher rubber concentration was responsible for the fall in tensile property beyond 15 wt%. Chain-slippage mechanism which could be responsible for the rubber-matrix adhesion and could also be hindered which justified the above phenomenon. Tensile modulus at maximum elongation was more up to 15 wt% after which values decreased indicating detachment of particles and creation of flaw particles.

Table 2 Thermal behaviour of isothermally cured resole (s) / epoxy / CTPB with different concentration of CTPB (heating rate 10°C/min)

Code	T_o (°C)	T_{max} (°C)	T_F (°C)	Mass loss (%)	T_o (°C)	T_{max} (°C)	T_F (°C)	Mass loss (%)	Char yield (%)
	I-Stage				II-Stage				
EC_0R_1	353	399	413	64.5	463	477	511	22.7	12.8
EC_5R_1	358	404	421	51.8	480	488	502	29.9	18.3
$EC_{10}R_1$									
$EC_{15}R_1$	346	381	384	39.5	475	485	574	46.6	13.9
$EC_{20}R_1$									
$EC_{25}R_1$	352	392	407	54.0	481	488	514	33.2	12.8
EC_0R_2	344	373	398	69.5	458	473	595	20.4	10.1
EC_5R_2	348	386	403	53.7	444	480	511	26.9	19.4
$EC_{10}R_2$									
$EC_{15}R_2$	358	394	410	58.7	433	437	453	28.6	12.7
$EC_{20}R_2$									
$EC_{25}R_2$	349	388	449	75.4	474	487	500	17.5	7.1
EC_0R_3	338	378	395	58.7	425	444	500	27.0	14.3
EC_5R_3	351	421	501	88.0	–	–	–	–	12.0
$EC_{10}R_3$									
$EC_{15}R_3$	352	408	439	47.1	483	500	517	43.8	9.1
$EC_{20}R_3$									
$EC_{25}R_3$	342	400	425	40.5	470	483	501	50.7	9.8
EC_0R_4	349	378	395	58.0	411	462	507	28.5	13.5
EC_5R_4	349	428	494	87.9	–	–	–	-	12.1
$EC_{10}R_4$									
$EC_{15}R_4$	340	396	417	63.2	467	480	517	24.7	12.1
$EC_{20}R_4$									
$EC_{25}R_4$	335	410	425	52.3	481	488	503	36.9	10.8

Table 3 Mechanical Properties of blend samples

Code	Tensile properties			Flexural properties		Impact Strength (kJ/m^2)	Fracture toughness (MPa m$^{1/2}$)
	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation-at-break (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)		
EC_0R_1	25.0	1.17	1.5	19.76	1.03	13.76	0.16
EC_5R_1	50.4	1.18	3.1	20.34	1.09	15.62	0.19
$EC_{10}R_1$	64.4	1.20	3.0	24.63	1.11	22.27	0.21
$EC_{15}R_1$	82.1	1.28	3.1	30.45	1.19	45.61	0.25
$EC_{20}R_1$	26.7	1.19	1.5	21.32	1.16	07.11	0.23
$EC_{25}R_1$	25.4	1.06	2.0	10.43	1.10	14.48	0.20
EC_0R_2	32.6	1.23	1.3	24.51	1.12	14.56	0.12
EC_5R_2	54.9	1.26	1.5	27.92	1.19	17.89	0.15
$EC_{10}R_2$	82.5	1.31	1.7	31.71	1.26	26.34	0.24
$EC_{15}R_2$	102.2	1.43	2.0	39.66	1.32	54.11	0.36
$EC_{20}R_2$	96.8	1.35	2.7	22.34	1.24	21.33	0.31
$EC_{25}R_2$	37.4	1.28	2.8	12.14	1.18	16.91	0.27
EC_0R_3	37.1	1.51	1.5	38.22	1.39	14.43	0.19
EC_5R_3	44.1	1.69	1.5	42.56	1.58	19.51	0.22
$EC_{10}R_3$	97.0	2.13	1.5	46.34	2.01	29.23	0.33
$EC_{15}R_3$	118.8	2.80	2.2	56.67	2.65	58.67	0.51
$EC_{20}R_3$	98.0	1.46	3.5	32.45	1.37	23.79	0.43
$EC_{25}R_3$	23.5	1.32	0.9	16.83	1.14	18.38	0.38
EC_0R_4	10.4	0.92	1.0	12.34	0.92	16.66	0.06
EC_5R_4	16.0	1.61	1.1	14.31	0.98	20.07	0.08
$EC_{10}R_4$	40.9	1.07	0.9	16.66	1.03	23.38	0.08
$EC_{15}R_4$	72.2	1.12	1.5	20.58	1.14	31.64	0.12
$EC_{20}R_4$	55.8	1.04	1.3	11.42	1.09	27.42	0.10
$EC_{25}R_4$	21.2	0.96	0.8	8.11	1.05	18.13	0.07

Flexural properties of the blend systems again showed an increasing trend up to 15 wt% of CTPB (Table 3) which was due to a uniform three-dimensional dispersion network system. The rise in flexural strength from neat to 15 wt% was found to be increased in the range of 48–66% as the type of resole, in the blend, was changed as compared to respective neat blend counterparts. This might be attributed to the percolation of rubber particles around the periphery of the polymer chains in the matrix resins. This percolated polymer chains enhanced the stress dissipation between the phase components during growth of the fracture. Intimate contact between the phases also enhanced the stored energy density and correspondingly the failure properties were improved. Beyond 15 wt% rubber content might increase the shear deformation which predominated along with more cavitations and segregation of particles which resulted a corresponding fall in flexural strength and modulus values.

Table 3 clearly indicated that all modified resole/epoxy networks exhibited higher impact resistance than non-modified resole/epoxy matrix. The best performance was normally achieved with 15 wt% of rubber. Above this optimum rubber content, a fall in the impact strength was observed. Similar behaviour has also been reported in other rubber-modified epoxy systems and attributed to the agglomeration of rubber particles with the increase of the rubber concentration [15, 22]. The presence of agglomerates acted as defects and initiated catastrophic failure. It has to be mentioned here that, impact test is very sensitive to voids, bubbles, and inclusions in the specimens. With the unnotched specimens, the stress does not concentrates on a specific point, and the material fractured at the weakest point, e.g., bubbles. So the impact strength of the specimens may not be in conformity with tensile test results. It may be concluded that, the best improvement in impact strength has been obtained with 15 wt% CTPB modification and with *p*-cresolic resole / epoxy matrix. This increased impact strength may also be correlated with the toughness improvement.

The data on plane strain fracture toughness (K_{IC}), from Table 3, revealed that the values of K_{IC} for unmodified resole / epoxy blend systems were comparatively low, reflecting the poor crack resistance of the matrix systems. In contrast, the CTPB-modified matrix resins gave values of K_{IC} that were greater than for the unmodified resole/epoxy blends over the complete range of present investigation. A closer investigation of these results showed that all fracture toughness values were remarkably low compared to those reported in the literature for CTBN-modified epoxy resins [23–27]. The origin of the problem appeared to be the preparation of the pre-crack in the fracture toughness specimens [27] or due to the presence of resole moieties in the blend itself. Table 3 also revealed that the values of K_{IC} showed an increasing trend with CTPB addition up to 15 wt%. Beyond 15 wt%, a fall in the values of K_{IC} was observed. The increase in the K_{IC} values might be attributed to the percolation of rubber particles around the polymer chains of the matrix resins. This ultimately enhanced the stress dissipation between the phase components during growth of the fracture. Intimate contact between the phases also enhanced the stored energy density and correspondingly the failure properties.

Morphological studies

The SEM micrographs of the neat and modified epoxy networks containing 5, 10, 15 and 25 wt% of CTPB have been shown in Fig. 5. The SEM micrograph of fractured surface of neat resole-epoxy blend (Fig. 5a) showed a paraboloid or clam shaped fracture which indicated brittle failure. The addition of 5 wt% CTPB into epoxy matrix did not cause any major changes in the morphological features. However, the addition of 10 wt% of CTPB in epoxy matrix started the formation of rubber globules (Fig. 5b). These rubber globules present in the matrix might act as stress absorbers and enhanced the toughness properties. Hindrance offered by these dispersed particles in the path of the fracture propagation resulted in increase in both tensile and the tensile modulus values up to 15 wt% CTPB (Fig. 5c). With increasing CTPB content, epoxy occlusion inside the rubber might occur and increased the size of the rubber particles. Further increase of CTPB, e.g., at 25 wt% (Fig. 5d), phase coalescence resulted an abrupt increase in the disperse phase size of 20 μm. Partial restriction in the smooth propagation of the fracture fronts due to both epoxy occlusion as well as phase growth might be the reason for a corresponding fall in the strength properties beyond a 15 wt% CTPB.

Conclusions

Resole–epoxy network modified with CTPB displayed two phase—separated morphology with dispersed rubber globules in the matrix resin. These dispersed particles showed hindrance in the path of the fracture propagation which resulted in increase in tensile strength and modulus, impact strength, plane strain

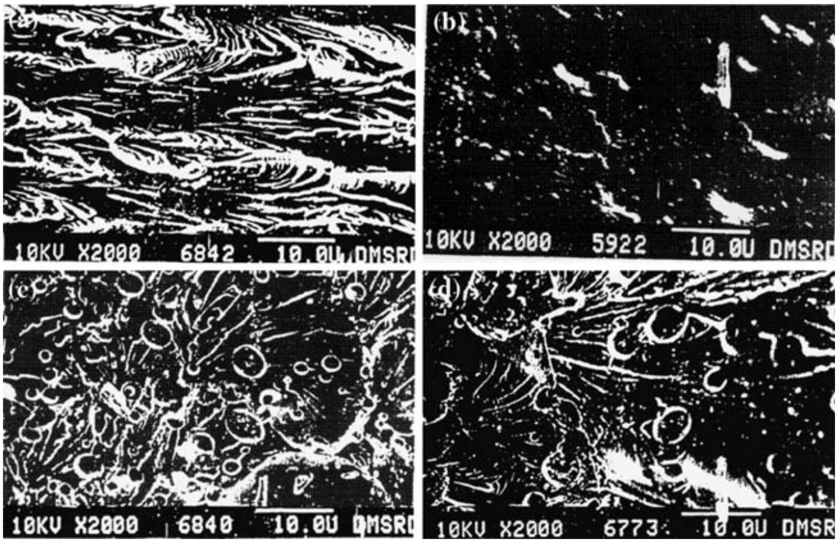


Fig. 5 SEM micrographs of (**a**) pure *p*-cresolic resole/epoxy blend and blend with (**b**) 5 wt% CTPB (**c**) 15 wt% CTPB and (**d**) 25 wt% CTPB

fracture toughness (K_{IC}) and flexural properties. This behaviour also increased the thermal stability of the blend systems.

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References

1. May CA, Tanaka GY (1973) Epoxy resin chemistry and technology. Marcel Dekker, New York
2. Kim JK, Robertson RE (1992) J Mater Sci 27:161
3. Frigione ME, Mascia L, Acierno D (1995) Eur Polym J 31:1021
4. Riew CK, Rowe EH, Siebert AR (1976) Adv Chem Ser 154:326
5. Sultan JN, McGarry FJ (1973) Polym Engg Sci 13:29
6. Visconti S, Marchessault RH (1974) Macromolecules 7:913
7. Sasidharan AP, Latha PB, Ramaswamy R (1990) J Appl Polym Sci 41:151
8. Verchere D, Pascault JP, Sautereau H, Moschiar SM, Riccardi CC, Williams RJJ (1991) J Appl Polym Sci 42:701
9. Verchere D, Sautereau H, Pascault JP, Moschiar SM, Riccardi CC, Williams RJJ (1990) J Appl Polym Sci 41:467
10. Bartlet P, Pascault JP, Sautereau H (1985) J Appl Polym Sci 30:2955
11. Chen TK, Jan YH (1991) Polym Engg Sci 31:577
12. Ratna D, Banthia AK (2000) Polym Int 49:281
13. Ratna D, Banthia AK (2000) Polym Int 49:309
14. Ratna D, Banthia AK, Deb PC (2000) J Appl Polym Sci 78:716
15. Ratna D, Banthia AK, Deb PC (2001) J Appl Polym Sci 80:1792
16. Drake RS, Egan DR, Murphy WT (1982) Am Chem Soc Org Coating, J Appl Polym Sci Proc 46:46
17. Nigam V, Saraf MN, Mathur GN (1997) J Thermal Analysis 29:483
18. Shukla SK, Srivastava D (2003) Intl J Plast Tech 7:32
19. Lee H, Neville K (1967) Handbook of epoxy resins. McGraw Hill, New York
20. Kinloch AJ, Kodokian GA, Jamarani MB (1987) J Mat Sci 22:4111
21. Barcia FL, Amaral TP, Soares BG (2003) Polymer 44:5811
22. Latha PB, Adhinarayanan K, Ramaswamy R (1994) Intl J Adhes Adhes 14:57
23. Bellenger V, Dahoui W, Verdu J, Galy J, Won TG, Pascault JP (1989) Polymer 30:2013
24. Tcharkhtchi A, Trotignon JP, Verdu J (1999) Macromol Symp 147:221
25. Pascault JP, Sautereau H, Verdu J, Williams RJJ (2002) Thermosetting polymers. Marcel Dekker, New York, p 350
26. Drzal LT (1986) Adv Polym Sci 75:4
27. Devanne T, Bry A, Audouin L, Verdu J (2005) Polymer 46:229