Blends of Modified Epoxy Resin and Carboxyl-Terminated Polybutadiene. I

Shailesh Kumar Shukla, Deepak Srivastava

Department of Plastic Technology, H. B. Technological Institute, Kanpur 208 002, India

ABSTRACT: Six blend samples were prepared by the physical mixing of epoxidized resole (EDR) with different weight ratios of carboxyl-terminated polybutadiene (CTPB) liquid rubber ranging from 0 to 25 wt % in intervals of 5 wt %. The formation of various reaction products during the curing of unblended EDR and CTPB-blended EDR were studied with Fourier transform infrared spectroscopy. The curing time at 100°C for the blend sample containing 15 wt % CTPB was the least among all of the blend samples. This blend sample, also, showed the highest initial degradation temperature, as obtained from thermogravimetric analysis thermograms, which indicated that it was the most thermally stable matrix system. The films of coatings based on the blend of EDR with 15 wt % CTPB offered the highest resistance toward different concentrations of acids and al-kalis compared to the films having 5, 10, 20, and 25 wt % CTPB in the EDR/CTPB blends. Solvents showed almost the same behavior as acids and alkalis for these films except for hydrocarbon solvents such as mineral turpentine oil, toluene, and xylene. The resistance toward these solvents was poor and slightly inferior to those found with EDR un-blended with CTPB. The tensile, flexural, and impact strengths of the molded specimens derived from the EDR/CTPB blends initially increased up to 15 wt % CTPB addition in the blend and then decreased, whereas the elongation at break remained constant for all blend compositions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1802–1808, 2006

Key words: infrared spectroscopy; polyamides; polybutadiene; strength; thermogravimetric analysis (TGA)

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting resins, with several outstanding characteristics, but they have the disadvantage of being relatively brittle.[1] This results in low impact resistance and low toughness, which limits the usage of epoxy resins. The toughness of epoxies is enhanced by the incorporation of a second phase, such as reactive liquid rubber, without a significant loss in other properties. This also improves the impact resistance of the epoxy resins. In this way, carboxyl-terminated poly-(acrylonitrile-*co*-butadiene) (CTBN) rubber,[2–5] acrylic elastomers,[6,7] and silicone rubber,[8] used as toughening elastomers, and polyimides and poly(ether ether ketone),[9–12] used as toughening thermoplastics, have been used successfully to prepare blends and to improve the toughness of epoxy resins.

Carboxyl-terminated polybutadiene (CTPB) is an indigenously available low-cost reactive liquid polymer that is mainly used in composite rocket propellants as a binder.[13,14] Blending epoxy resin and CTPB may also produce toughened composites. These blends might show better strain to failure and, hence, high energy-absorbing characteristics. The composites may be suitable for the purpose of high-energy-absorbing innovative applications for the latest version of the space shuttle, rocket technology, missile technology, transportation, and so on. In this investigation, we prepared blends of epoxidized resole (EDR) and CTPB and studied their mechanical and thermal properties.

EXPERIMENTAL

Phenol, formaldehyde, sodium hydroxide (all laboratory reagent grade, M/s Thomas Baker Chemicals, Ltd., Mumbai, India) were used for the preparation of the resole. Epichlorohydrin (M/s Qualigens Fine Chemicals, Mumbai, India) was used for the epoxidation of the resole. Polyamide (amine value = 240–400 mg of KOH/g) was procured from M/s Parikh Resins, Ltd. (Naya Ganj, Kanpur, India) to cure the EDR and its blends with CTPB (acid value = 27.37 g of KOH/g). CTPB was procured from Vikram Sarabhai Space Research Centre (VSSRC; Thiruvananthapuram, India) as a gift sample.

The resole was synthesized by a method similar to the method adopted by Knop and Scheib.[15] Approximately 94 g (1 mol) of distilled phenol was reacted with 164 g of aqueous formaldehyde (37 wt %, 2.0 mol) and 10.4 g of sodium hydroxide (4% of the total

Correspondence to: D. Srivastava, 34-A, Vikas Nagar, Kanpur 208 024, India (deepak_sri92@rediffmail.com).

TABLE I
Sample Designations

Sample	EDR (wt %)	CTPB (C; wt%)	Sample designation
1	100	0	S-0
2	95	05	S-5
3	90	10	S-10
4	85	15	S-15
5	80	20	S-20
6	75	25	S-25

TABLE II
Variation of Curing Time[a] with CTPB Addition in the Blends of EDR and CTPB

		Curing time	
Sample	Sample designation	Without curing agent	With curing agent
1	S-0	60	48
2	S-5	50	34
3	S-10	50	32
4	S-15	48	26
5	S-20	50	34
6	S-25	50	36

[a] Cured at 100°C with and without 40 wt % polyamide.

charge of phenol and formaldehyde) in a 500-mL, three-necked round bottomed (RB) flask equipped with a reflux condenser, a stirrer, and a siphoning tube that led to a collecting trap for the removal of samples for testing during the reaction. The reaction mixture was stirred and heated in an oil bath at 70°C for 2–2.5 h. The pH and free formaldehyde content were checked every 15 min throughout the reaction. Two layers were formed when stirring was stopped. A sufficient 10% sulfuric acid was added to bring the pH to 6–7. The water formed during the reaction was evaporated with a vacuum film evaporator under reduced pressure (30–35 mm of Hg).

Approximately 282 g of resole resin was mixed with 140 g of epichlorohydrin in a three-necked RB flask with a reflux condenser and a mechanical stirrer in an oil bath at 70°C for 2 h. After the completion of the reaction, the contents of the flask were neutralized with a 25% sulfuric acid solution up to a pH of 7.0. Finally, the sample was dried at 80°C under reduced pressure (30 mm of Hg) to obtain the desired product. The epoxide-equivalent weight was 180 equiv/g of KOH.[16] The EDR was mixed physically with various concentrations of CTPB ranging between 0 and 25 wt %. All of the sample designations are given in Table I.

Fourier transform infrared (FTIR) spectra of all of the blend samples were recorded with a Bruken Victor

IR spectrophotometer (Billerca, MA) (model 2.2) in the wavelength range 200–4000 cm^{-1} with a computerized recorder. For this, the blend sample and cerium iodide were ground in a ratio of 1 : 4 and then placed into an IR pellet die at 40 psi to obtain the pellets. These pellets were placed near the window of the FTIR spectrophotometer.

We determined the cure schedule of the blend samples in a hot-air oven by heating the samples for different temperatures and times. For the sake of simplicity, we kept the temperature constant, that is, at 100°C, and heated the samples for different time periods to determine the cure times of the blend samples with polyamide (40 wt % of the total weight of the blends of EDR and CTPB) as a curing agent.[17,18] The cure temperature for pure resole was taken from differential scanning calorimetry (TA Instruments, Inc., model 2910, New Castle, DE) under the dynamic mode, and this was considered a basis for the cure temperature for the different blend systems through the air oven. The related data for different blend samples are given in Table II.

The thermal stability was determined by a comparison of the onset degradation temperature (5% weight loss) of the cured samples with thermogravimetric analysis (TGA; DuPont, model TGA VSIA DuPont 2100, New Castle, DE) at a heating rate of 10°C/min and in a nitrogen atmosphere with a flow rate of 10 cc/min from ambient temperature to 800°C. The data obtained from the TGA curves are summarized in Tables III and IV.

TABLE III
Temperatures for 1–10% Weight Loss as Measured by TGA of the Cured Blend Samples

Weight loss (%)	Temperature (K)					
	S-0 (min)	S-5 (min)	S-10 (min)	S-15 (min)	S-20 (min)	S-25 (min)
1	344	418	420	390	348	352
2	433	482	485	440	399	404
3	496	558	498	505	468	482
4	543	588	523	566	546	563
5	563	596	597	599	596	595
6	574	609	610	613	611	609
7	593	618	619	622	618	616
8	600	622	624	631	623	621
9	606	626	630	640	631	633
10	613	635	642	659	634	637

TABLE IV
IDT Values at 5% Weight Loss of Blends of EDR and CTPB Coatings as Measured by TGA

Sample	Sample designation	IDT (°C)	Char yield (%)
1	S-0	290	20.0
2	S-5	323	23.6
3	S-10	320	24.0
4	S-15	326	24.8
5	S-20	323	18.6
6	S-25	322	14.8

	Period (months)					
Acid or alkalie	S-0	S-5	S-10	S-15	S-20	S-25
10% sulfuric acid	5	7	7	11	10	8
25% sulfuric acid	5	7	7	11	8	8
10% hydrochloric acid	5	7	6	11	7	7
25% hydrochloric acid	4	6	5	10	6	5
10% nitric acid	5	8	7	12	8	7
25% nitric acid	4	7	6	11	7	7
10% sodium hydroxide	8	10	9	>12	11	10
25% sodium hydroxide	7	7	6	11	8	7
10% potassium hydroxide	8	10	9	>12	11	10
25% potassium hydroxide	6	7	7	11	8	8
10% ammonium hydroxide	8	8	7	12	10	10
25% ammonium hydroxide	7	7	6	11	8	10

We prepared the panels by applying the blends of EDR and CTPB samples on sand-blasted steel sheet panels 150 × 100 × 1.25 mm in size with a Bird film applicator (Sheen Instruments, Ltd., Surrey, UK). These panels were further sealed on three sides with molten paraffin wax. A dry film thickness of about 150 μm was maintained on all the panels. These films were then cured as per the cure schedule determined earlier. The panels were examined for visible changes in the conditions of the film samples at regular intervals when immersed in different chemicals such as solvents, acids, and alkalis at ambient temperature for a period of 12 months. The observations taken during the studies are summarized in Tables V and VI.

Dumbbell-shaped cured samples (size = 7.5 × 3/4 × 1/8 in.) of the EDR/CTPB blends were used for the determination of tensile strength and elongation at break according to the ASTM D 638 standard in a universal testing machine (Patiwana Group, Star Testing Systems, Mumbai, India). The crosshead speed of the machine was kept at 25 cm/min. Rectangular-shaped samples (size = 5 × 1/2 × 1/8 in.) of the epoxidized/CTPB blends were used for the determination of flexural strength according to ASTM D 190–63 specifications. The crosshead speed of the universal testing machine was kept at 25 cm/min. The impact strength of the cured samples (size = 2.5 cm × 1 cm × 1/8 in. with notch) of the blend samples was measured with an Izod impact tester (M/s W & T Avery, Ltd., Birmingham, England).

RESULTS AND DISCUSSION

The synthesized phenolic resole and its epoxidation reactions were analyzed by FTIR analysis and were reported elsewhere.[19] The following structure of EDR may be proposed, as per the discussion given in ref. 19:
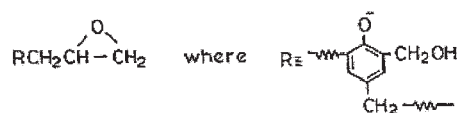
The IR spectra of the blend samples containing 0–25 wt % CTPB in EDR are shown in Figure 1. As shown in Figure 1, the characteristic peaks of oxirane ring functionality of the epoxy at 910 and 880 cm^{-1} appeared at low levels of CTPB addition in the blends (e.g., blend samples S-5 and S-10). Also, there appeared two bands of peaks near 1700–1725 cm^{-1} and 1550–1610 cm^{-1}, which might have been due to carbonyl stretching of carboxylic acid (—COOH) and carboxylate anion stretching, respectively, for blend samples S-5 and S-10. These peaks disappeared as the concentration of CTPB was increased to 15 wt % in the blend (sample S-15; Fig. 1). Further, these peaks appeared with low intensities in the spectrum of sample S-25. The disappearance of these peaks and the simultaneous appearance of a new stretched peak near 1300–1400 cm^{-1}, due to carboxylate anions, in the blend sample S-15 clearly indicated the occurrence of a chemical reaction between the epoxy and CTPB. However, an insufficient rubber content in the blend samples (S-5 and S-10) could not completely consume the epoxide groups of the EDR and, thus, showed the peaks near 910 and 880 cm^{-1}. At higher levels of CTPB addition, although the epoxy groups disappeared completely, the unreacted carboxylic acid groups showed its presence along with the ester crosslinks.

On the basis of the previous discussion, it could be inferred that the presence of carboxylic acid groups or carboxylate anions in the blends of EDR and CTPB might have behaved as a curing agent for such blend systems. The chemical reactions given in Scheme 1 are proposed. The reaction product (A) might have fur-

TABLE VI
Comparative Solvent Resistances of the Films of the Blends of EDR with CTPB During the Period After Which the First Effect Was Detected When the Sample was Immersed for 12 Months at Ambient Temperature

Solvent	Period in months					
	S-0	S-5	S-10	S-15	S-20	S-25
Deionized water	9	10	10	11	11	11
Synthetic sea water	8	10	10	11	11	11
Methanol	7	8	10	11	1	10
Acetone	7	8	9	11	11	8
Methyl ethyl ketone	7	7	8	11	10	8
Toluene	7	5	6	6	5	4
Xylene	7	5	5	6	5	4
MTO	8	6	6	7	6	4

ther reacted with epoxide or carboxylate groups, as shown in Scheme 2.

Products A, B, or C might have reacted with polyamide and finally resulted in a crosslinked product.

As shown in the preceding reactions, curing proceeded in the presence of CTPB but at a slower rate due to the formation of products such as C, which did not react further either with epoxide or carbonyl
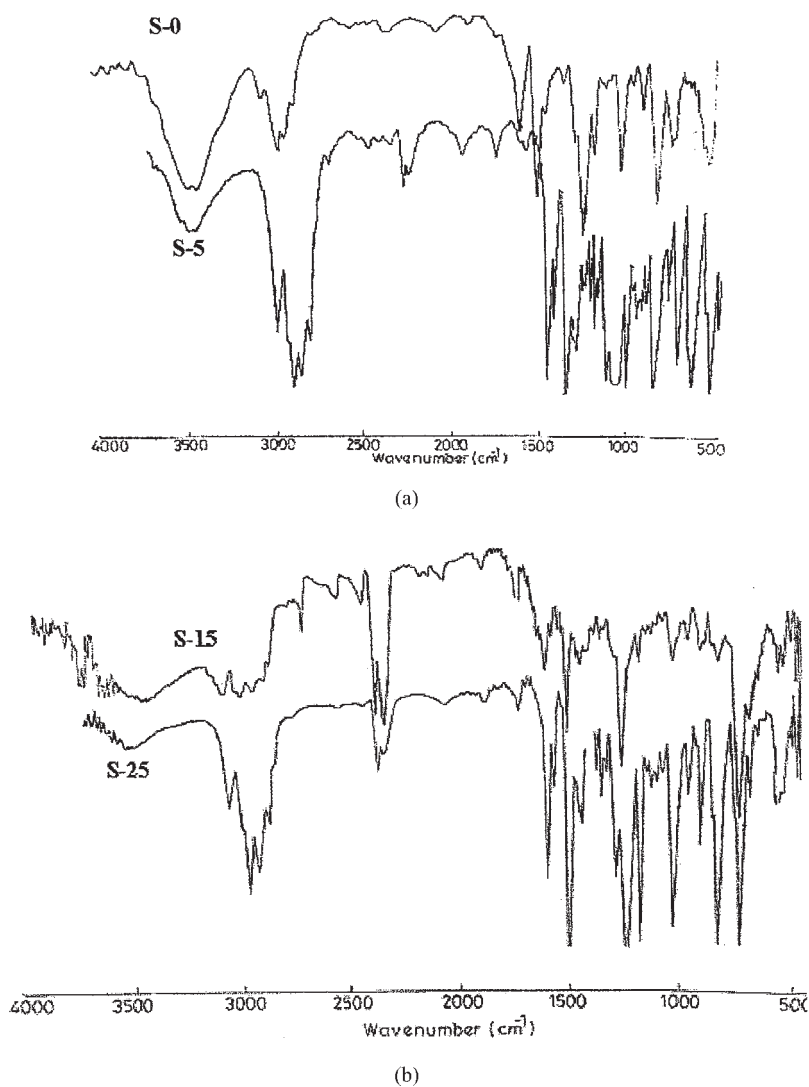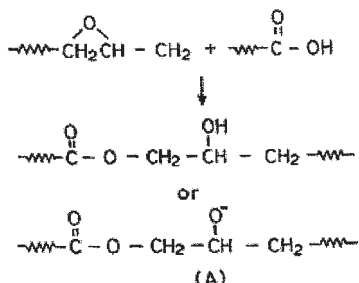

(a)

(b)

Figure 1 FTIR spectra of samples (a) S-0 and S-5 and (b) S-15 and S-25.
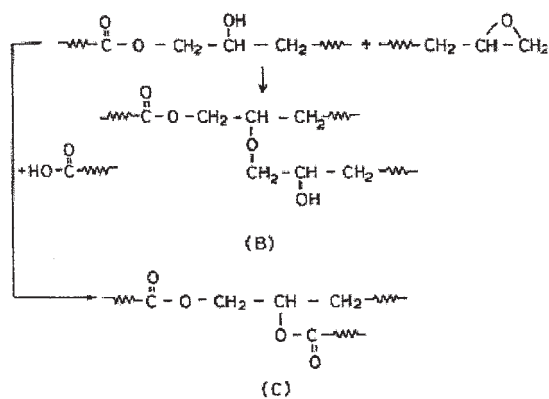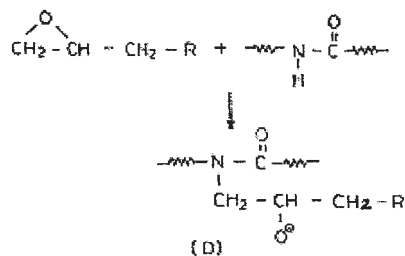
Scheme 1

Scheme 3

groups. This was further confirmed by the results of the cure times of the blend samples (Table II).

On the basis of the previous discussion, the reaction of epoxide groups with polyamide are proposed, as shown in Scheme 3. Product D might have further reacted with another epoxide group, as shown in Scheme 4, and so on. Finally, a crosslinked (cured) product resulted. A similar mechanism was proposed by Chen et al.[20] and Blainvaux et al.[21] for the curing reactions of epoxy and CTBN.

The temperatures of 1–10% weight loss in the TGA curve at a heating rate of 10°C/min for the cured EDR/CTPB blend samples are given in Tables III and IV. From the temperature for a particular degree of weight loss, it is apparent that the thermal stability of the blend sample containing 15 wt % CTPB was the greatest among the blend samples containing 5–25 wt % CTPB. The temperature up to 5 wt % loss in TGA thermograms was ignored, as these might have appeared due to presence of impurities in the blends. Thus, the temperatures for 5% weight loss were treated as indicating temperatures for the thermal stability of the blends, and these temperatures are shown in Table IV. As shown in Table IV, the blend sample containing 15 wt % CTPB showed the highest initial degradation temperature (IDT), 326°C, among all of the blend samples containing 5–25 wt % CTPB. Also, the percentage char yield was highest for sample S-15

(Table IV). The blend sample without CTPB (S-0) showed the lowest IDT (290°C) and char yield (20%).

The formation of more thermally stable blend samples (S-15) might be attributed to the presence of aromatic content and the formation of more crosslinks in the cured blend sample.

The comparative acid and alkali resistance of the films of the EDR/CTPB blends are summarized in Table V. A quick perusal of Table V clearly illustrates that the film of coatings based on blends of EDR with 15 wt % CTPB offered the highest resistance toward different concentrations of acids and alkalis compared to the films with 5, 10, 20, and 25 wt % CTPB in the EDR/CTPB blends. This behavior was attributed to the behavior and structure of CTPB. At concentrations greater than 15 wt %, CTPB might have shown a dispersed phase morphology between EDR and CTPB, which resulted in a slightly inferior performance. The comparative resistance of the films of different blends of EDR and CTPB against different solvents are shown in Table VI. Table VI reveals almost similar behavior, as shown with the acids and alkalis, except for with hydrocarbon solvents, such as mineral turpentine oil (MTO), toluene, and xylene. The resistance toward these solvents was poor and slightly inferior to those found with EDR unblended with CTPB. This might have been due to the structure of rubber, which might have given dispersed phases of EDR and CTPB and, hence, reduced the solvent resistance.

The variation of tensile strength, elongation at break, flexural strength, and impact strength with
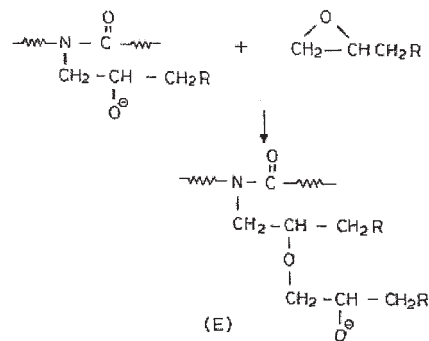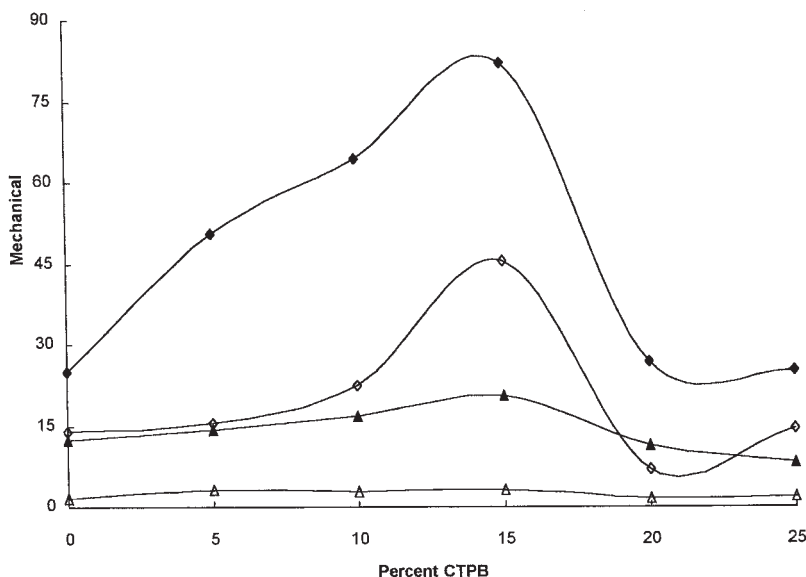

Scheme 2

Scheme 4

Figure 2 Variation of the mechanical properties of the blends of EDR and CTPB: (♦) tensile strength (MPa), (▲) flexural strength (MPa), (△) elongation at break (%), and (◇) impact strength (kJ/m²).

CTPB content in the blend samples of EDR and CTPB cured with 40% polyamide are shown in Figure 2.

The tensile strength of the blend samples increased up to a 15 wt % addition of CTPB in the blend and then decreased. Elongation at break was marginally affected by the CTPB content in the blend. The initial increase in the tensile strength of the blend samples with CTPB addition might have been due to restricted plastic deformation by well-dispersed CTPB particles. The results were quite similar to those of Nigam et al.[14] and Kushenbaum and Bell[22] on epoxy cresol novolac resin and CTPB blends. They observed that there occurred the propagation of several small tiny fracture fronts with occasional formation and termination inside the fractured zone due to the hindrance offered by rubber particles and cavitations of the rubbery domains. Because of a brighter phase boundary surrounding the rubber, the particles presented the development of compatibility between CTPB with the thermoset due to interaction. An increase in tensile properties, therefore, might have indicated some kind of interaction between the CTPB particles with EDR and the formation of a complete matrix, which might have been mechanically stronger than thermoset alone. Above 15 wt % CTPB addition, the previously mentioned mechanical perspective and deformation pattern might have altogether been changed. A similar discussion was given by Wang and Zukko[23] on CTBN and diepoxy blends. They concluded that there initially existed one phase system in all of the blend samples of CTBN and epoxies. During the cure the phase, separation occurred in competition with network formation. The two processes were responsible for the final morphology. Beyond 15 wt %, in our case,

the tensile strength decreased, which might be explained by the rubber particle (CTPB) morphology and the structural changes of the network.[24] This phenomenon might be interpreted with the stress concentration affect[25] of the rubber particles. The decrease in the tensile strength was explained in a different way by Yee and Pearson.[26] According to their theory, at higher rubber contents, many small rubber particles might exist between the larger ones, and the effect of the rubber particle interaction with each other might be more than that of simple replacement of the matrix by a certain volume fraction of low-strength and low-modulus material. They also concluded that there might be the onset of a shear-flow process even before the maximum stress is reached and that this would show a small deviation in the elongation at break. Our results were similar, as is clear from Figure 2.

The flexural strength initially increased by about 9.5% compared with EDR (Fig. 2) as 5 wt % CTPB was added in the blend of EDR and CTPB. When 15 wt % CTPB (S-15) was added in the blend, the value of flexural strength increased by about 68% compared with EDR. After this, the value of flexural strength decreased by about 61% up to 25 wt % CTPB in the blends.

It is evident from Figure 2 that the impact strengths of the CTPB-modified EDR blends were significantly greater than that of the unmodified EDR. This might have arisen from the main energy-dissipating micromechanisms at the crack tip involving shear deformations in the EDR blends. This analogy was drawn on the basis of work done by Kinolch et al.[4,5] The extent of such deformations might have been very limited in the unmodified material but occurred over 15 wt %

CTPB addition in the blends because many such deformations were limited by the CTPB particles present in the multiphase polymer. Many workers[26–32] have interpreted such results on the basis of increased plastic and viscoelastic energies. These might dissipate at the crack tip by these multiple deformations, which reflect an increase in the values of impact strength. Beyond 15 wt % CTPB addition in the blends, the impact strength decreased, which might have been due to dissolution of the CTPB particles in the blend of EDR and the CTPB matrix.[32]

CONCLUSIONS

From the preceding results and discussion, we concluded that the blends of EDR and CTPB showed an increase in tensile strength, flexural strength, and impact strength up to 15 wt % CTPB addition in the blends and a decrease thereafter, whereas the elongation at break remained constant for all of the blend samples. The cure time of the samples decreased up to 15 wt % addition of CTPB in the blends and then decreased. The solvents affected the films of such blends almost in the same manner as they were affected by acids and alkalis except for hydrocarbon solvents, such as MTO, toluene, and xylene. The thermal stability of the blend sample containing 15 wt % CTPB was higher than that of EDR.

References

1. Kum, S.; Kim, J.; Jo, W. H.; Choe, C. R. J Appl Polym Sci 1999, 72, 1055.
2. Hunston, D. L.; Bascom, W. B. In Rubber-Modified Thermoset Resins; Rao, C. K.; Gillham, J. K., Eds.; ACS Symposium Series 208, American Chemical Society: Washington, DC, 1984; p 83.
3. Ting, R. Y. In Epoxy Resins; May, C. A., Ed.; Marcel Dekker: New York, 1988; p 551.
4. Kinloch, A. J. In Rubber-Toughened Plastics; Riew, C. K., Ed.; Advances in Chemistry Series 22; American Chemical Society: Washington, DC, 1989; p 67.
5. Kinloch, A. J.; Shaw, S. J.; Hunston, D. L. Polymer 1983, 24, 1355.
6. Iijima, T.; Tomoi, M.; Suzuki, A.; Kakiuchi, H. Eur Polym J 1991, 27, 851.
7. Ochi, M.; Yamashita, K.; Shimbo, M. Kobunshi Ronbunshu 1988, 45, 817.
8. Kasemura, T.; Kawamoto, K.; Kashima, Y. J Adhes 1990, 33, 19.
9. Bucknall, C. B.; Gilbert, A. H. Polymer 1989, 30, 213.
10. Nishi, S.; Sasaki, S.; Hasuda, Y. Polym Prepr (Am Chem Soc Div Polym Chem) 1987, 28, 175.
11. Hedrick, J. L.; Yilgor, I.; Wilkes, G. L.; McGrath, J. E. Polym Bull 1985, 13, 201.
12. Yamanaka, K.; Inoue, T. Polymer 1989, 30, 662.
13. Drake, R. S.; Egan, D. R.; Murphy, W. T. Chem Soc Org Coating, J Appl Polym Sci 1982, 46, 46.
14. Nigam, V.; Saraf, M. N.; Mathur, G. N. J Therm Anal 1997, 29, 483.
15. Knop, A.; Scheib, W. In Chemistry and Application of Phenolic Resins; Springer-Verlag: Berlin, 1979.
16. Lee, H.; Neville, K. In Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
17. Shukla, S. K.; Srivastava, D. Ind J Chem Tech 2001, 8, 357.
18. Shukla, S. K.; Srivastava, D. Mater Manuf Processes 2001, 16, 281.
19. Shukla, S. K.; Srivastava, D. Int J Plast Tech 2003, 7, 32.
20. Chen, D.; Pascault, J. P.; Bertsch, R. J.; Drake, R. S.; Siebert, A. R. J Appl Polym Sci 1994, 51, 1959.
21. Blainvaux, F. L.; Madec, P. J.; Marechal, E. J Polym Bull 1985, 13, 237.
22. Kushenbaum, S. L.; Bell, J. P. J Appl Polym Sci 1989, 24, 2571.
23. Wang, T. T.; Zukko, M. M. J Appl Polym Sci 1981, 26, 2391.
24. Bartlet, P.; Pascault, J. P.; Santereau, H. J Appl Polym Sci 1985, 30, 2955.
25. Bascom, W. O.; Vottington, R. L.; Jones, R. L.; Peyser, P. J Appl Polym Sci 1975, 19, 2545.
26. Yee, A. F.; Pearson, R. A. J Mater Sci 1986, 21, 2462.
27. Pearson, R. A.; Yee, A. F. J Mater Sci 1989, 24, 2571.
28. Kushenbaum, S. L.; Bell, J. P. J Appl Polym Sci 1985, 30, 1875.
29. Kinloch, A. J.; Kodokian, G. A.; Jamarani, M. B. J Mater Sci 1987, 22, 4111.
30. Pearson, R. A.; Yee, A. F. J Mater Sci 1986, 21, 2475.
31. Kinloch, A. J.; Show, S. J.; Tod, D. A.; Hunston, D. L. J Polym 1983, 24, 1341.
32. Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. J Appl Polym Sci 1991, 43, 293.