Use of Acrylate-Based Liquid Rubbers as Toughening Agents and Adhesive Property Modifiers of Epoxy Resin

Sritama Kar, Ajit K. Banthia

Materials Science Centre, Indian Institute of Technology, Kharagpur, Kharagpur 721302, India

Received 16 July 2003; accepted 21 November 2003

ABSTRACT: Carboxyl-randomized poly(2-ethyl hexyl acrylate) (CRPEHA) and epoxy-randomized poly(2-ethylhexyl acrylate) (ERPEHA) were synthesized by solution polymerization technique in the form of liquid rubbers. The liquid rubbers were characterized by IR and ^{1}H-NMR spectroscopic analysis, nonaqueous titration, and GPC. The liquid rubbers were pre-reacted with the epoxy resin and the modified epoxy networks were made by curing with an ambient temperature curing agent. The modified epoxy networks containing different concentrations of CRPEHA (A-1) and ERPEHA (B-1) were evaluated with respect to their thermal and impact properties. The optimum properties were obtained at 10-phr concentration of a (1 : 1) mixture of CRPEHA and ERPEHA. Fracture surface analysis by scanning electron microcopy indicated the presence of a two-phase microstructure. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3814–3821, 2004

Key words: epoxy; CRPEHA; ERPEHA; impact; adhesion; toughened; microstructure; aluminum; wood; voids; shear yielding; plastic deformation; cavitation

INTRODUCTION

Epoxy resins are a class of versatile polymer materials that form networks on curing and are used as structural adhesives. This is due to their high wetting ability, good mechanical properties (viz., high modulus and tensile strength), high chemical resistance, and high temperature service capability [weight loss of resin cured with 4,4′-diaminodiphenyl methane (DDM) when heated in air at 175°C for 16 h was only about 0.1%].[1,2] However, when cured with a stoichiometric amount of polyfunctional amines, the high degree of crosslinking makes the cured epoxy network a very brittle material. It weakens the epoxy's peel and impact strengths and, therefore, limits its application. Hence, modification of epoxy resin has been the subject of immense interest.

Considerable work has been carried out to improve the toughness of an epoxy resin by inclusion of (1) flexible long-chain hardeners, such as polyamide and polysulfide[3]; (2) long aliphatic epoxy chain[4]; and (3) compatible polymers, for example, epoxy-nylon and epoxy-phenolic systems.[5]

Since the early 1970s, the elastomer-toughened epoxy resins, especially nitrile-epoxy[6] and carboxyl-terminated acrylonitrile-butadiene liquid polymer (CTBN)-epoxy[7–13] systems, were viewed as potential high-performance adhesives because of their durability and ability to prevent catastrophic failure of the structural joints. The theory[14] is that the reactive liquid rubber having functional end-groups reacts with the epoxy resin. During the initial stage, it will be compatible with epoxy-hardener mixture. As the curing reaction proceeds, the molecular weight increases and phase separation occurs at a certain stage because of the entropy effect,[15] leading to the formation of a two-phase microstructure. Such a two-phase system having rubber particles dispersed and bonded to epoxy matrix shows a very high crack resistance without significant deterioration of other thermomechanical properties.[8–14] Recently, epoxidized triglycerides were investigated to modify epoxy resins.[16] Ochi and Bell have synthesized carboxyl-terminated poly(*n*-butyl acrylate) by using carboxyl-ended initiator and chain transfer agent by bulk polymerization technique and have successfully used it as an effective toughening agent for epoxy resin/methylene dianiline system.[17] Pocius and Wilson have carried out considerable work for improvement of adhesive bond strengths of epoxy resins.[18,19]

In our present work, we have developed cured epoxy adhesive formulations by using carboxyl-randomized poly(2-ethylhexyl acrylate) (CRPEHA) and epoxy-randomized poly(2-ethylhexyl acrylate) (ERPRHA) as tougheners. The present article discusses the evaluation of modified epoxy networks containing different concentrations of CRPEHA (A-1) and ERPEHA (B-1), with respect to their thermal, and impact and adhesive properties.

Correspondence to: A. K. Banthia (abanthia@hotmail.com).

Journal of Applied Polymer Science, Vol. 92, 3814–3821 (2004)
© 2004 Wiley Periodicals, Inc.

TABLE I
Physicochemical Properties of CRPEHA and ERPEHA

Liquid rubbers	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Carboxyl content (mmol g^{-1})	Epoxy content (g mol^{-1})	Carboxyl functionality (eq mol^{-1})
CRPEHA (A-1)	3900	1.52	0.404	—	1.68
ERPEHA (B-1)	4100	1.61	0.0114	4000	0.046

EXPERIMENTAL

Materials

Liquid rubbers CRPEHA (A-1) and ERPEHA (B-1) were used as toughening agents in the present work. The monomers, 2-ethylhexyl acrylate (EHA), acrylic acid (AA), and glycidyl acrylate (GA), were obtained from Fluka (Buchs, Switzerland). Thioglycolic acid (TGA) (Aldrich, Milwaukee, WI) and benzoyl peroxide (BPO; BDH, Mumbai, India) were used as chain transfer agent and initiator, respectively.

The epoxy resin was a liquid diglycidyl ether of bisphenol-A type (Ciba Geigy, Araldite LY 556) with an equivalent weight per epoxide group of 195 ± 5. Triphenyl phosphine (TPP) (SISCO, Mumbai, India) was used as catalyst for carboxyl-epoxy reaction. Triethylene tetramine (TETA; Ciba Geigy; HY 951) was used as curing agent.

Synthesis of liquid rubbers

Copolymer CRPEHA was synthesized by solution polymerization of EHA and AA (10 mol %) monomer mixture (100 g), using BPO (500 mg) as initiator, 5 mol % TGA (1.66 mL) as chain transfer agent, and dioxan (150 mL) as solvent in the presence of nitrogen gas at 99°C. The product was washed with water to remove the solvent and traces of TGA, if any, and then was centrifuged and heated at 80°C to remove the water. Copolymer ERPEHA was synthesized by following the same procedure as above but by using GA (5 mol %) in place of AA.

The carboxyl content of CRPEHA was determined by titration with methanolic solution of 0.1*N* KOH by using phenolphthalein as indicator. The functionality (*f*) of CRPEHA was calculated by multiplying the carboxyl content, expressed in mol/g, with the number-average molecular weight. Functionality is as expressed as eq/mol.[20]

The epoxy content of ERPEHA was determined by titration with HBr in acetic acid by using crystal violet as indicator.[20]

Molecular weights and polydispersity indices of CRPEHA and ERPEHA oligomers were determined by gel permeation chromatography (GPC), using an interphase module system from Water Associates. Microstyragel was used as the column material, and THF was the eluting solvent. The molecular weight was determined by using polystyrene standard.

IR spectra of the samples were obtained with a Perkin–Elmer spectrometer at a resolution of 2.4 cm^{-1}. The spectra of liquid polymer samples were recorded as neat between KBr discs. ^{1}H-NMR spectroscopy was carried out by using Bruker AC-200 spectrometer at 200 MHz with $CDCl_3$ solvent.

Modification of epoxy and curing

Epoxy resin was pre-reacted with liquid rubbers before curing. The required amount of epoxy resin was pre-reacted with A-1, B-1, and a mixture of A-1 and B-1 by stirring in the presence of TPP catalyst at 80°C for 3 h to obtain formulations of different compositions (Table I).

All the compositions of epoxy resin pre-reacted with liquid rubber were subsequently cured by adding TETA in a stoichiometric amount (26 g per equivalent of epoxy group). The mixture was cast into an aluminum mold and cured at room temperature (25°C) for 2 days. The samples were postcured at 80°C for 2 h.

Characterization of modified epoxy networks

Dynamic mechanical analysis (DMA) was carried out for cured epoxy samples by a dynamic mechanical analyzer (DMTA MK III, Rheometric Scientific) at a fixed frequency of 1 Hz with a 3°C/min heating rate by using liquid nitrogen for subambient region. Dynamic moduli and loss factors were obtained in a dual-cantilever mode for the sample of size 14 × 10 × 2 mm.

The Izod unnotched impact bulk test was carried out according to ASTM D 4812-93 specifications by using an impact tester with a striking velocity of 3.35 m s^{-1}. Impact test specimens in all cases were 125 × 10 × 10 mm^3. The impact test was carried out at 25°C and impact energy was reported in J m^{-1}. Five test samples were used for each formulation.

Single-lap shear strength was determined for aluminum–aluminum (B 51 SWP) bonds according to ASTM D-1002 standard by using aluminum sheets of size 8.89 × 2.54 cm with an overlap of 2.54 cm. The thickness of the sheets was 1.6 mm. The adhesive formulation was applied uniformly on both the surfaces to be mated and these were mated by using contact pressure and cured. The adhesive layer was 0.03 mm thick and the coating length was 1.27 cm longer than the adhering length. The joint strength was measured in a universal testing machine (Zwick 4308) after 7 days of bonding. The crosshead speed of 20 mm/min was used for lap shear strength measurements[21] at 25°C. Five replicates were used per adhesive formulation.

A scanning electron microscope (SEM; JEOL, JSM-5800) was used to analyze the failure surfaces (sheared in the lap shear strength determination) of the toughened adhesive network joints. The surface of the sheared joint was mounted on an aluminum stub by using a conductive (silver) paint and was sputter coated with gold. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Characterization of liquid rubber

CRPEHA (A-1) oligomer (i.e., copolymer of EHA and AA) was synthesized by solution polymerization by using BPO as an initiator and TGA as chain transfer agent at 99°C. ERPEHA (B-1) oligomer (i.e., copolymer of EHA and GA) was also synthesized by following the same procedure as above. A-1 and B-1 were characterized by IR and ^{1}H-NMR spectroscopic analysis. In the IR spectrum, A-1 shows peaks at 1735 cm^{-1} and at 1398 cm^{-1}, which are due to the carboxyl ester group and to carboxylate anion stretching, respectively. B-1 shows peaks at 819 and 876 cm^{-1}, which are due to the epoxy group.

A peak at 2.1 ppm in the NMR spectra of A-1 indicates the presence of —COOH group attached to an alkyl proton and in the spectra of B-1, peaks at 2.5, 2.7, and 3.1 ppm indicate the presence of epoxy groups. Detailed study of this spectroscopic analysis is available in our previous article.[20]

The physicochemical properties of A-1 and B-1 are summarized in Table I, from which it is evident that the molecular weight and polydispersity index of B-1 are greater than those of A-1. The carboxyl content of rubber A-1 is 0.404 mmol g^{-1} and that of B-1 is 0.0114 mmol g^{-1}. The epoxy content of ERPEHA is 4000 g mol^{-1}. The functionality of rubber A-1 is 1.68 eq mol^{-1}.

Pre-reaction of liquid rubbers with epoxy and curing

For effective toughening, the liquid rubbers need to be chemically bonded to the epoxy matrix.[22,23] In addition, an accumulation of free liquid rubber molecules at the metal adherent surface can act as a weak boundary layer in the adhesive joint leading to a substantial decrease in adhesive joint strength.[11,24] The liquid rubber was always pre-reacted with the epoxy resin before adding the hardener. The reaction rate of hardener with the epoxy is much faster and thus may block the reaction sites of the epoxy so the rubber will not completely react and the toughening effect will be less pronounced. The addition of rubber first to the resin will prevent this problem. For this reason, before curing, the epoxy resin was pre-reacted with (A-1), (B-1), and mixtures of A-1 and B-1 in the presence of TPP as a catalyst until no carboxyl groups were present. The reaction is basically a carboxyl-epoxy esterification reaction, as proposed by Romanchick et al.[25] and as shown in Figure 1.

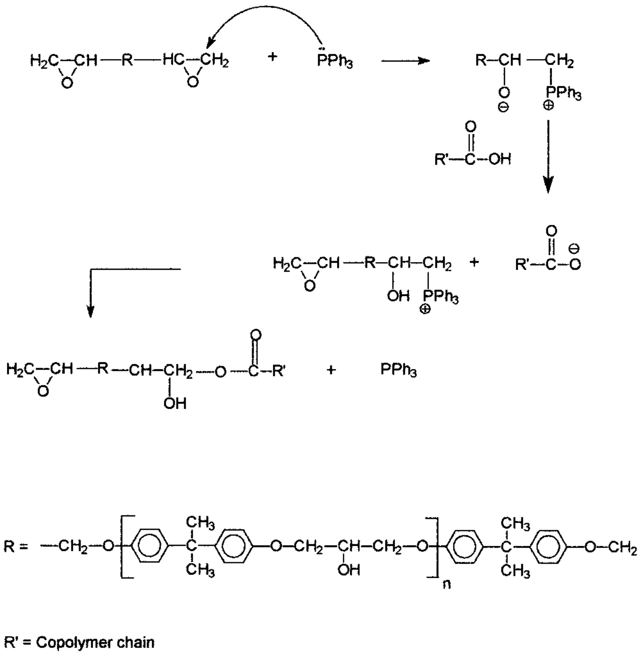

Figure 1 Mechanism of triphenyl phosphine catalyzed carboxyl-epoxy reaction.

The product was a carboxyl-randomized poly(2-ethylhexyl acrylate)-epoxy copolymer, which is capable of reacting with the hardener in the same way as epoxy. The modified sample was liquid and no solidification or gelling was observed after pre-reaction. The diluted mixture was then cured with HY 951 to obtain the crosslinked networks. The probable mechanism is shown in Figure 2.

Characterization of modified networks

The modified networks containing different concentrations of CRPEHA and ERPEHA were evaluated for their thermal and impact properties to study the effect of the modifier concentration on the properties of the

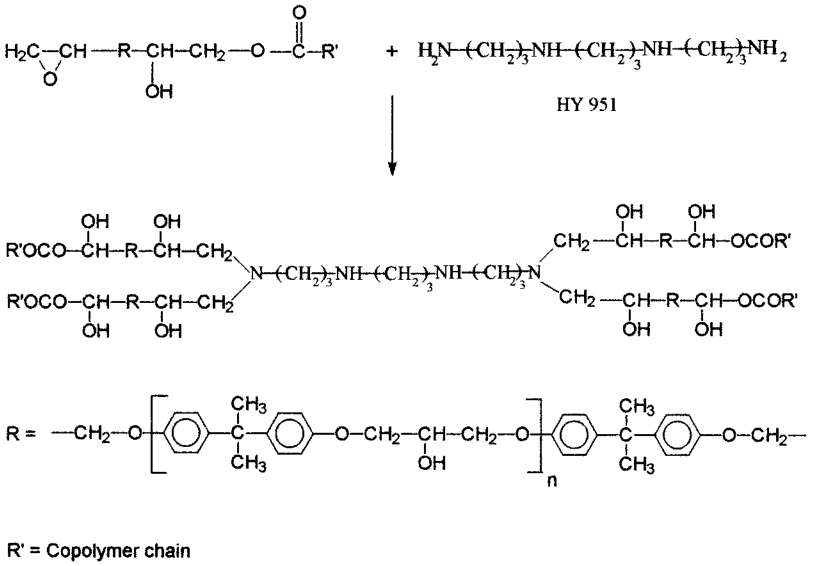

Figure 2 Curing reaction of liquid rubber modified epoxy with HY 951 (TETA).

modified networks. Various compositions of epoxy resin/(A-1 and B-1 in 1 : 1 ratio) by varying the liquid rubber concentration are shown in Table II. In Table III, compositions of epoxy/10 phr liquid rubber (containing A-1 and B-1 in different ratios) are shown.

Impact properties of modified networks

The toughening effect is reflected in the increase in impact strength as a result of incorporation of liquid rubber in the adhesive formulation. The effect of incorporation of liquid rubbers A-1 and B-1 on the impact strength of modified networks is shown in Tables IV and V. From these two tables, it is evident that highest impact strength is achieved for a composition of epoxy/10 phr liquid rubber (1 : 1 mixture of A-1 and B-1). Approximately a fivefold increase in impact strength was achieved for this (S-5) composition. A twofold increase of impact strength was reported for epoxy/CRPEHA system.[20] The epoxy/A-1 and B-1 system containing both dissolved (B-1) and phase-separated (A-1) rubbers can form strong interfacial bonds with the epoxy matrix. Hence, for S-5 composition, both the toughening and the flexibility effects can be operative, resulting in maximum improvement in impact strength.

S-7 is a single-phase system containing only dissolved rubber, evident from the DMA studies. The dissolved rubber imparts flexibility to the rigid matrix and improves the impact strength by initiating plastic deformation. Hence, the S-7 shows higher impact strength than the S-3 system.

Effect of liquid rubber modification on the joint strength bonded with epoxy adhesives

To study the effect of liquid rubber modification on the adhesive properties of epoxy, various formulations were made by incorporating different concentrations of liquid rubbers (1 : 1 of CRPEHA and ERPEHA).

The lap shear strengths of epoxy adhesive formulations for Al–Al and wood–wood joints measured after postcuring are given in Figures 3 and 4, respectively. Improvement in adhesive bond strength was reported

TABLE II
Compositions of Epoxy Resin and Liquid Rubbers (1 : 1)

Sample	CRPEHA + ERPEHA (phr)	Epoxy resin
S-1	0	100
S-2	2.5	100
S-3	5.0	100
S-4	7.5	100
S-5	10	100
S-6	15	100
S-7	20	100

TABLE III
Compositions of Epoxy Resin and Liquid Rubbers (10 phr)

Sample	CRPEHA : ERPEHA (10 phr)	Epoxy resin
S-5_A	0 : 10	100
S-5_B	2.5 : 7.5	100
S-5	5 : 5	100
S-5_C	7.5 : 2.5	100
S-5_D	10 : 0	100

TABLE IV
Impact Strength of Liquid Rubbers (1 : 1) Modified Epoxy Networks at Varying Concentrations

Sample	Impact strength (J/m)
S-1	70
S-2	100
S-3	160
S-4	230
S-5	360
S-6	310
S-7	280

by many authors by using CTBN liquid rubber as a modifier.[26–29] Ramamurty and coworkers[30] reported a threefold increase in lap shear strength by using carboxyl-terminated poly(propylene glycol) adipate as liquid rubber. Ratna and Banthia reported a twofold increase in lap shear strength by using carboxyl-terminated poly(2-ethylhexyl acrylate) (CTPEHA) as the liquid rubber.[31] The value of lap shear strength for Al–Al joints for the S-5 composition was 5.17 MPa (Fig. 3). In our previous article, it was reported that the value of lap shear strength for the Al–Al joints bonded with aluminum silicate filled A-1 and B-1 (1 : 1) modified samples was 6.32 MPa.[20]

The value of lap shear strength for wood–wood joints for the S-5 composition was 9.85 MPa, which is about 1.89 times the value for unmodified epoxy (Fig. 4). The carboxyl groups of A-1 pre-react with the epoxy groups of both ERPEHA and epoxy resin, as well as the hardener at the interface is also expected to react with epoxy groups of both epoxy resin and ERPEHA. Thus, chemical bonds are formed between the rigid matrix and rubber particles, which is necessary for effective toughening[15,30,32] and thus prevents or minimizes the catastrophic failure of structural bonds. The epoxy/(A-1 and B-1) system has both dissolved and phase-separated rubbers (B-1) and (A-1) and can form strong interfacial bonds with the epoxy matrix, which results in better stress transfer across the interface. There is a flexibilizing effect on the matrix, which causes shear yielding of the matrix at low stress and hence enhances toughness. In the case of S-5, the rubber particles are smaller and more uniformly dispersed than that in S-5_C and S-5_D, resulting in better toughening due to greater stress concentration caused by smaller particles. In the case of S-5_A and S-5_B, phase separation has not taken place because of the greater compatibility of B-1 with the epoxy resin because of the presence of the glycidyl groups; consequently, the rubber particles cannot act efficiently in dissipating mechanical energy.[20] This explains why S-5 formulation has the highest adhesive strength for both the Al–Al and the wood–wood joints.

TABLE V
Impact Strength of (10 phr) Liquid Rubbers Modified Epoxy Networks at Varying Ratios of Liquid Rubbers

Sample	Impact strength (J/m)
S-1	70
S-5_A	90
S-5_B	290
S-5	360
S-5_C	320
S-5_D	170

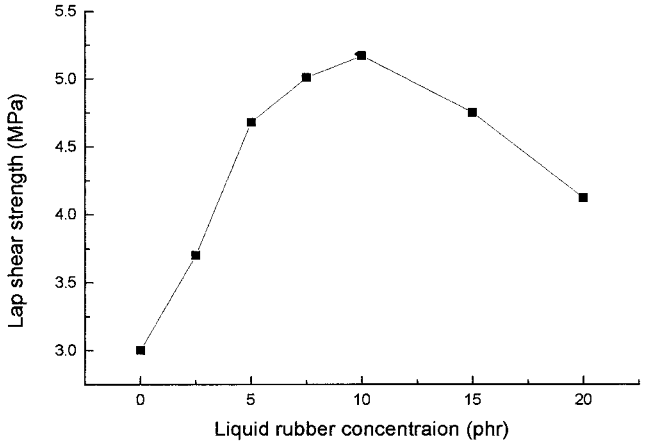

Figure 3 Effect of liquid rubber modification on the lap shear strength (Al–Al joints) of epoxy resin.

Thermal analysis

To study the effect of incorporation of liquid rubbers on the viscoelastic properties of a modified epoxy network, the pure epoxy and modified epoxy network containing CRPEHA and ERPEHA (1 : 1) were subjected to DMA analysis from 30 to 150°C. All the

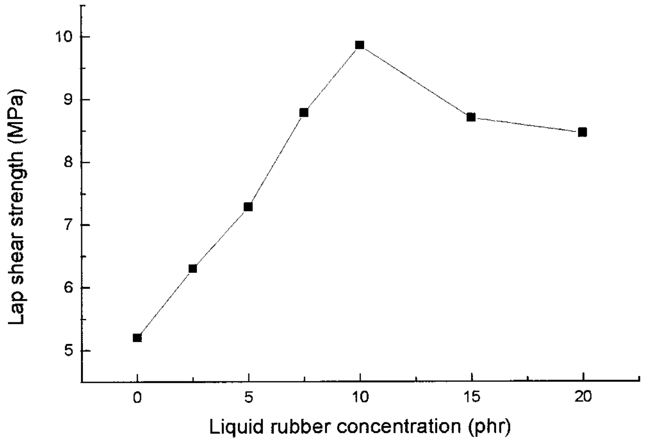

Figure 4 Effect of liquid rubber modification on the lap shear strength (wood–wood joints) of epoxy resin.

TABLE VI
DMTA Analysis of Liquid Rubbers Modified Networks

Resin	Storage modulus (MPa)	tan δ peak temperature (°C)	tan δ_{max}
S-1	953	147.48	0.38
S-3	906	145.05	0.44
S-5	627	139.15	0.51
S-7	596	134.32	0.47

modified networks show one transition peak. From the DMTA spectra, the values of storage modulus (E') at 60°C, tan δ_{max}, and tan δ peak temperature were obtained and reported in Table VI. The effect of liquid rubber concentration on high-temperature relaxation peak is shown in Figure 5, which represents the loss factor (tan δ) plots against temperature for pure and liquid rubber modified epoxy networks. The peak is attributed to the α relaxation of the unmodified epoxy. From the results, it is evident that the storage modulus (E') at 60°C and the tan δ peak temperature gradually decreases with the increase of liquid rubbers (A-1 and B-1) concentration and maximum depression was observed for the S-5 composition. The dynamic modulus (E') also follows the same trend as tan δ (Fig. 6). (E') is greatest for the S-3 system and smallest for the S-7 system. However, all the blends exhibit a higher tan δ_{max} in comparison with the pure epoxy, indicating better dissipation of mechanical energy and hence higher impact strength. This can similarly be explained on the basis of the dual role of S-5 in imparting both the flexibility and the toughening characteristics to the resultant epoxy networks.

Scanning electron microscopy analysis

To correlate the morphological parameters with the fracture properties of the toughened epoxy resins, the microstructures of the fracture surfaces of various rubber-modified epoxy resin were analyzed by SEM. The micrographs for rubber-modified resin are shown in Figure 7. The fracture surface of the unmodified epoxy [Fig. 7(a)] is homogeneous without any dispersed particles. It further confirms the brittle nature of the fracture process in the unmodified cured epoxy resins.

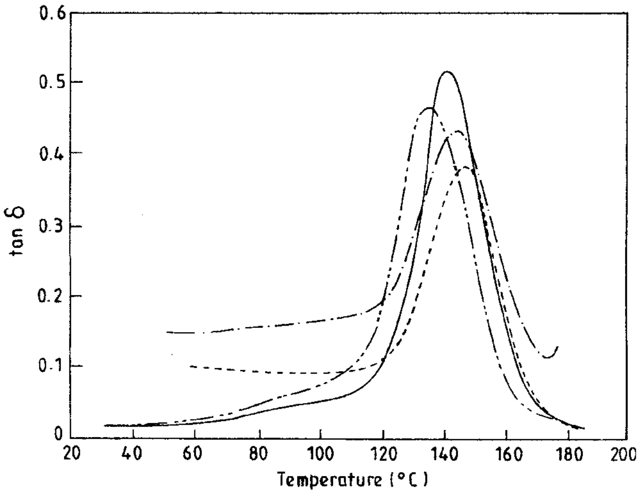

Figure 5 High-temperature relaxation of unmodified epoxy (· · ·), S-3-modified networks epoxy (– • –), S-5-modified networks (—), S-7-modified networks (– • • –).

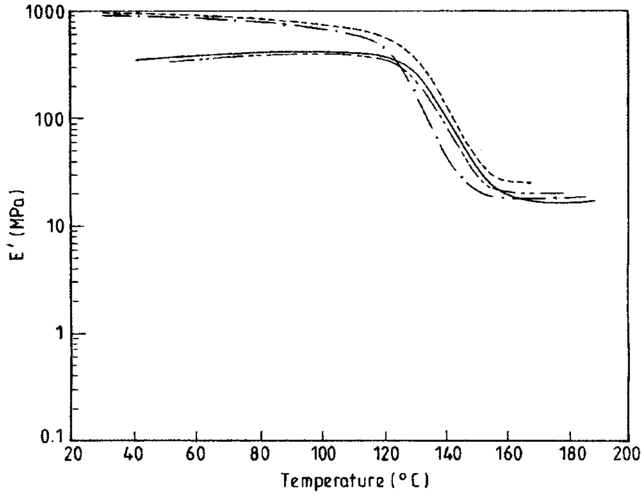

Figure 6 Storage modulus versus temperature plot of unmodified epoxy (· · ·), S-3-modified networks (– • –), S-5-modified networks (—), S-7-modified networks (– • • –).

The fracture surfaces of the S-5 liquid rubber modified epoxy resins [Fig. 7(c, d)] consist of two distinct phases; globular rubber particles are distributed throughout the continuous epoxy matrix. The rubber particles are uniformly distributed throughout the matrix. The particles have dimensions in the range of 1–6 μm, and their distribution is bimodal in nature. In the micrographs, one can see the stress-whitened zone. The stress-whitened zone is due to the scattering of visible light from the layer of the scattering center—in this case, voids.[33,34] The generation of these voids is due to the cavitations of the rubber particles, and the matrix surrounding the voids exhibits notable plastic deformation as evidenced by the beveled edge of the voids. Also, there is clear evidence of shear banding between rubber particles, which suggests appreciable matrix shear yielding and plastic deformation over a large volume. This is the primary cause for energy absorption mechanism in the case of rubber-toughened epoxy.[35] The aggregation starts at a higher concentration. This explains why the impact and adhesion properties attain a maximum value at about S-5 and subsequently decreases.

The poor fracture property of the S-3 liquid rubber modified epoxy resins [Fig. 7(b)] can also be explained by considering the morphology as observed in the SEM. The SEM photograph indicates the presence of large particles (>10 μm) distributed haphazardly. The

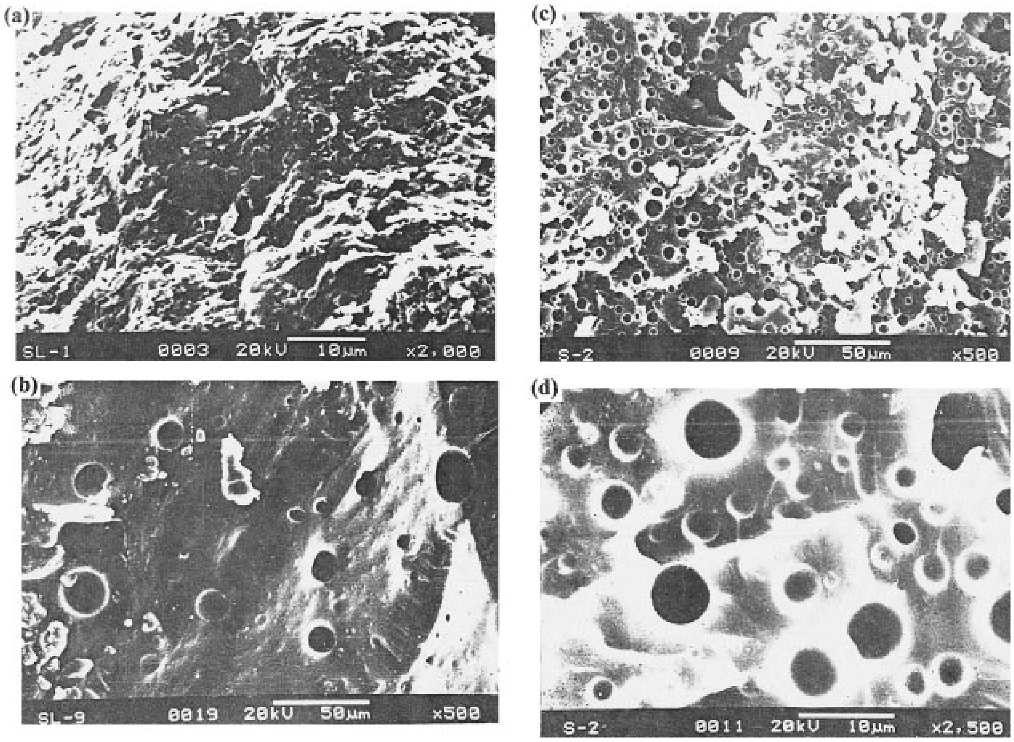

Figure 7 SEM photographs of the fracture surfaces of (a) unmodified epoxy, (b) S-3-modified networks, (c) S-5-modified networks, and (d) S-5-modified networks at higher magnification.

larger particles cannot act efficiently in dissipating mechanical energy but instead act as defects[36,37] and thereby reduce the impact strength.

CONCLUSION

The liquid rubbers CRPEHA and ERPEHA, when prereacted with epoxy resin and cured by using a hardener HY 951, impart the plasticizing and toughening effect. CRPEHA and ERPEHA were prepared by solution polymerization technique. These liquid rubbers used as modifiers (tougheners) for epoxy resin and the formation of a two-phase system were confirmed from the SEM micrographs of failure surfaces after the lap shear test.

The liquid rubbers were evaluated as a toughening agent for epoxy resin with respect to their thermal properties, impact and adhesive joint strength of the modified networks. Our results showed that maximum improvement in impact strength could be achieved by incorporating the liquid rubbers in 1 : 1 ratio at a concentration of 10 phr into the epoxy matrix.

References

1. Potter, W. G. Epoxide Resins; Springer-Verlag: New York, 1970.
2. May, C. A.; Tanaka, G. Y., Eds. Epoxy Resins: Chemistry and Technology; Marcel Dekker: New York, 1973.
3. Peters, R. A.; Logan, T. J. Adhes Age 1975, 18, 17.
4. Ratna, D.; Banthia, A. K.; Deb, P. C. J Appl Sci 2001, 80, 1792.
5. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967; Chapter 21, pp 1–49.
6. Morris, C. E. M.; Pearce, P. J.; Davidson, R. G. J Adhes 1982, 15, 1.
7. Riew, C. K. Rubber Chem Technol 1985, 58, 622.
8. Bascom, W. D.; Cottington, R. L.; Jones, R. L.; Peyser, P. J Appl Polym Sci 1975, 19, 2545.
9. Manzione, L. T.; Gillham, J. K.; McPherson, C. A. J Appl Polym Sci 1981, 26, 889.
10. Bascom, W. D.; Hunston, D. L. in Rubber Toughened Plastics; Riew, C. K., Ed.; ACS Symposium Series No. 222; American Chemical Society: Washington, DC, 1989; p 135.
11. Dodiuk, H.; Kening, S.; Liran, I. J Adhes 1987, 22, 227.
12. Achary, P. S.; Latha, P. B.; Ramaswamy, R. J Appl Polym Sci 1990, 41, 151.
13. Romano, A. M.; Garbassi, F.; Braglia, R. J Appl Polym Sci 1994, 52, 1775.
14. Bitner, J. L.; Rushfold, J. L.; Rose, W. S.; Hunston, D. L.; Riew, C. K. J Adhes 1981, 13, 3.
15. Scarito, P. R.; Sperling, L. H. Polym Eng Sci 1979, 19, 297.
16. Frischinger, I.; Dirlikov, S. Polym Mater Sci Eng 1993, 70, 1.
17. Ochi, M.; Bell, J. P. J Appl Polym Sci 1984, 29, 1381.
18. Pocius, A. V. Proc Int SAMPE Tech Conf 1987, 19, 312.
19. Pocius, A. V.; Wilson, T. H. Proc Int SAMPE Tech Conf 1987, 19, 177.
20. Kar, S.; Gupta, D.; Banthia, A. K.; Ratna, D. Polym Int to appear.
21. Kar, S.; Gupta, D.; Banthia, A. K. J Adhes Sci Technol 2002, 16 (14), 1901.
22. Iijima, T.; Naoto, Y.; Masao, T. Eur Polym Mater 1992, 28, 573.
23. Sohn, J. E. Org Coat Plast Chem 1981, 44, 381.

24. Xuzong, N.; Lijuan, W.; Rulian, X.; Yiming, L.; Yunchao, Y. Adhesive Chemistry: Development and Trends; Lee, L. H., Ed.; Plenum: New York, 1984; p 659.
25. Romanchick, W. A.; Sohn, J. E.; Gaibel, J. F. in Epoxy Resin Chemistry II; Bauer, R. S., Ed.; ACS Symposium Series No. 221; American Chemical Society: Washington, DC, 1983; p 93.
26. Bascom, W. D.; Cottington, R. L. J Adhes 0976, 7, 333.
27. Huange, H.; Kinloch, A. J. J Adhes 1993, 41, 5.
28. Hunston, D. L.; Kinloch, A. J.; Shaw, S. J.; Wang, S. S. in Adhesive Joints: Formation, Characteristics and Testing; Mittal, K. L., Ed.; Plenum: New York, 1984; p 789.
29. Nakao, K.; Yamanka, K. J Adhes 1992, 37, 15.
30. Achary, P. S.; Goury, C.; Ramamurty, R. J Appl Polym Sci 1991, 42, 743.
31. Ratna, D.; Banthia, A. K. Polym Int 2000, 49, 281.
32. Bucknall, C. B.; Yoshii, T. Br Polym J 1978, 10, 53.
33. Lee, W. H.; Hodd, K. A.; Wright, W. W. in Rubber Toughened Plastics; Riew, C. K., Ed.; Advances in Chemistry Series 222; American Chemical Society: Washington, DC, 1989; pp 263.
34. Kar, S.; Banthia, A. K. Pigment Resin Technol 2003, 32 (2), 69.
35. Kinloch, A. J.; Shaw, S. J.; Hunston, D. L. Polymer 1983, 24, 1355.
36. Pearson, R. A.; Yee, A. F. J Mater Sci 1989, 24, 2571.
37. Kunz-Douglass, S.; Beamount, P. W. R.; Ashby, M. F. J Mater Sci 1980, 15, 1109.