

Toughening of Epoxy Resin Using Acrylate-Based Liquid Rubbers

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ABSTRACT: Carboxyl-terminated poly(2-ethylhexyl acrylate) (CTPEHA) liquid rubbers of different molecular weights and functionalities (LR-1 to LR-6) were synthesized by bulk and solution polymerization techniques. The liquid rubbers were characterized by nonaqueous titration, vapor pressure osmometry, and gel permeation chromatography. The CTPEHA oligomers were prereacted with the epoxy resin, and the modified epoxy networks were made by curing with an ambient-temperature curing agent. The impact properties of the modified epoxy networks were evaluated, and the effects of molecular weight, functionality of the liquid rubber, and ductility of the matrix on the impact strength of the modified networks were investigated. The morphology of the toughening behavior was analyzed using a scanning electron microscope. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 716–723, 2000

Key words: epoxy; 2-ethylhexyl acrylate; toughening; modified epoxy

INTRODUCTION

Epoxy resins are unique among all the thermosetting resins because of several factors.^{1,2} For example, minimum pressure is needed for fabrication of products normally used for thermosetting resins; shrinkage is much lower, and hence there's lower residual stress in the cured product than that encountered when vinyl polymerization is used to cure unsaturated polyester resins; use of a wide range of temperatures is possible by judicious selection of a curing agent that has good control over the degree of crosslinking; and there's availability of resin types ranging from low-viscous liquids to tack-free solids. Because of these unique characteristics and useful properties of the network polymer, epoxy resins are widely used as structural adhesives, surface coat-

ings, engineering composites, electrical laminates, and so forth.^{1–3}

The major drawback of epoxy resin is its brittleness in the cured state, with a fracture energy about two orders of magnitude lower than that of engineering thermoplastics and three orders lower than that of metals.⁴ This inherent brittleness results in epoxy composites having poor damage tolerance from impact and in the poor peeling and shear strength of epoxy-based adhesives. Hence, modification of epoxy resins to impart fracture toughness has been the subject of intense research interest.

Following the work reported by McGarry and Willner⁵ that a reactive liquid rubber such as a carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) is useful for the fracture toughness of epoxy resins, much work has been reported in this field. The theory is that the liquid rubber reacts with epoxy through the reactive carboxylic functional groups. During the initial stage, the reactive liquid rubber is compatible

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with the epoxy-hardener mixture. As the curing reaction proceeds, the molecular weight increases, and at some stage phase separation occurs, leading to the formation of a two-phase morphology.⁷⁻⁹ Improvement in fracture toughness is achieved without a significant reduction in the thermal and mechanical properties of the crosslinked epoxy resin. However, since the butadiene component of the elastomers contains unsaturation, it would appear to be a site for premature thermal and/or oxidative instability, and such modified resins are not suitable for use at a high temperature.¹⁰ It can be imagined that excessive crosslinking could take place with time, which would detract from the otherwise desirable improvements accomplished with these structures. In addition, the possibility that traces of free acrylonitrile, a carcinogenic, might exist limits the use of these materials.¹¹ Moreover, most of the reported rubber-toughened epoxy formulations require heat cure. Heat curing is difficult and impractical for the fabrication of certain structures and requires a significant amount of energy. Ambient curing saves energy and is advantageous for surface-coating applications and adhesives to the intricate structures.

Recently, some saturated liquid rubbers such as polysulfide,¹² acrylate,^{13,14} silicone,⁵ and polyurethane¹⁶ have been reported in the literature as replacements for CTBN. We have used carboxyl-terminated poly(2-ethylhexyl acrylate) (CTPEHA) liquid rubber to toughen epoxy resin cured with an ambient temperature hardener. In the present article the effects of molecular weight, functionality of the liquid rubber, and the matrix ductility on the toughening of epoxy resin were investigated.

EXPERIMENTAL

Materials

The monomer 2-ethylhexyl acrylate (EHA) (Fluka) was purified by washing twice with sodium hydroxide solution to remove the inhibitors and then repeatedly washing with distilled water. It was then dried over anhydrous calcium chloride for 48 h. Recrystallized from ethanol, 4,4'-azobis(4-cyanovaleric acid) (ABCVA) (Aldrich) was used as a free radical initiator. Benzoyl peroxide (BPO) (BDH, India) was repeatedly recrystallized from chloroform prior to using as a free radical initiator and was stored at -25°C . Di-

Table I Chemical Structure of Epoxy Resin and Hardeners

Materials	Chemical Structure
Epoxy resin LY 556	<p style="text-align: center;">$n = 0.4$</p>
Hardener HY 951	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ Triethylene tetramine TETA
Hardener HY 960	<p style="text-align: center;">2,4,6-Tris(N,N-dimethyl amino methyl) phenol</p>

thiodiglycolic acid (DTDGA) (Aldrich) was used as a chain transfer agent without further purification. Triphenyl phosphine (TPP) (SISCO, India) was used as received. Solvents such as tetrahydrofuran (THF), toluene, dioxan, and methanol were of analytical grade (BDH, India).

The epoxy resin was a liquid diglycidyl ether of bisphenol A (Ciba Geigy, Araldite LY 556), with an equivalent weight per epoxide group of 195 ± 5 . Ambient temperature hardeners used were an aliphatic polyamine (Ciba Geigy, HY 951) and an aromatic amine (HY 960). The chemical structures of the epoxy resin and hardeners are given in Table I.

Synthesis and Characterization of Liquid Rubbers

CTPEHA oligomers with different molecular weights were synthesized by bulk polymerization using ABCVA as the free radical initiator and by varying the concentration of the chain transfer agent, DTDGA. The reaction was carried out in a three-necked reaction flask (500 mL) fitted with a stirrer, a thermometer pocket, and a gas inlet. Approximately 100 g (0.54 mol) of EHA monomer was taken into the reaction flask and was rapidly

brought to the desired temperature. After the system was well purged with nitrogen gas, 3.0 g of ABCVA (2 mol %) and the required amount of DTDGA (2.3–11.3 g, 2–10 mol %) were added, and the reaction was allowed to occur for 1 h with stirring. The mixture was then diluted with toluene (200 mL) and cooled to room temperature and kept overnight. The unreacted ABCVA and DTDGA precipitated out and were removed by filtration. Unreacted monomer and the solvents were removed under vacuum on a rotary evaporator until a constant weight was obtained.

A typical preparation by solution polymerization technique uses inhibitor-free monomer (100 g, 0.54 mol), ABCVA (3 g, 0.014 mol), DTDGA (11.3 g, 0.04 mol), and solvent (150 mL). The materials were introduced into a reaction flask (500 mL) fitted with a condenser and a gas inlet. Nitrogen gas was slowly bubbled through the reaction mixture for 15 min to remove the dissolved oxygen. The mixture was heated to reflux temperature and heated at reflux for 5 h. The solution was cooled and then filtered. Unreacted monomer and solvent were removed under vacuum on a rotary evaporator until a constant weight was obtained.

The carboxyl content of the CTPEHA oligomer was determined by titration with a methanolic solution of 0.10N KOH, using phenolphthalein as an indicator.

The viscosity was measured using a Haake Rotoviscometer (Haake RV III) at a shear rate range of 0–100 s⁻¹ at 27°C, using an MV III head having a clearance of 0.96 mm between the concentric cylinders of the viscometer.

The number-average molecular weights (M_n) of all the liquid rubbers were determined using a Knauer vapor pressure osmometer (VPO), with toluene as the solvent and benzil as a standard. Molecular weights and the molecular-weight distributions were determined from gel permeation chromatography (GPC), using an interphase module system from Water Associates. Microstyrigel was used as the column material, and THF was the eluting solvent. The molecular weights were determined using a polystyrene standard. The functionality (f) of the liquid rubber was calculated by multiplying the carboxyl content, expressed in eq/g with the number-average molecular weight. Functionality is expressed as eq/mol.

Modification of Epoxy and Curing

Epoxy resin (100 parts) was prereacted with 10 parts each of liquid rubber (LR-1–LR-6), using

TPP as the catalyst. The reaction was carried out at 80°C under nitrogen atmosphere until all the carboxyl groups were completely reacted. The modified epoxy networks were made by curing all the formulations with HY 951. In order to study the effect of matrix ductility on the toughening effect, an unmodified epoxy network and a modified epoxy network (with the liquid rubber having optimum molecular weight) were made using HY 960 as a curing agent. Hence, unless mentioned, hardener means HY 951.

All the formulations were analyzed for their epoxy content by standard titration¹⁷ with hydrogen bromide in acetic acid. Accordingly, a stoichiometric amount (26 g of HY 951 or 12 g of HY 960 for one equivalent of epoxy) of hardener was added and thoroughly mixed. The mixture was cast into a Teflon mold and cured at room temperature (RT) for 2 days. The samples were post-cured at 80°C for 2 h.

Characterization of Modified Networks

The Izod unnotched impact test was carried out using an Avery–Dennison impact tester with a striking velocity of 3.46 m/s. Impact test specimens in all cases were 125 × 10 × 4 mm³. The impact test was carried out at room temperature, and the impact energy was reported in J/m. The quoted result is the average of the determinations on 10 unnotched samples.

Fracture Surface Analysis

A low-voltage scanning electron microscope (SEM) (JEOL, JSM-840) was used to examine the fracture surfaces of the toughened epoxy samples. A thin section of the fracture surface was cut and mounted on an aluminum stub using a conductive (silver) paint and was sputter coated with gold prior to fractographic examination. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

Characterization of Liquid Rubbers

Four liquid rubbers (LR-1 to LR-4) of different molecular weight were synthesized using the same concentration of ABCVA (2 mol %) and varying amounts of DTDGA (2 to 10 mol %). The liquid rubbers were characterized by VPO and

Table II Physicochemical Properties of Liquid Rubbers (Synthesized by Bulk Polymerization)

Liquid Rubber CTPEHA	DTDGA (Conc. mol %)	\bar{M}_n^a	\bar{M}_n^b	\bar{M}_w^b/\bar{M}_n^b	Functionality (f) (eq/mol)
LR-1	2	9500	8000	7.8	1.8
LR-2	5	7000	4700	8.2	1.7
LR-3	8	5300	3700	9.8	1.8
LR-4	10	3600	2400	7.3	1.9

^a Measured by VPO.^b Measured by GPC.

GPC analysis for their molecular weights and molecular-weight distributions. The molecular weights and molecular-weight distributions are reported in Table II.

As expected from the principle of free radical polymerization,⁸ the molecular weight decreases with increased DTDGA concentration. The number average molecular weight (\bar{M}_n) reduced from 9500 to 3600 g/mol as the DTDGA concentration increased from 2 mol % to 10 mol %. The number-average molecular weights measured by VPO were higher than those measured by GPC. This can be attributed to the presence of carboxyl groups, which cause specific intermolecular interactions inside the GPC column. This interaction prolongs the retention time, which is inversely related to \bar{M}_n .

On dissociation, the initiator ABCVA generates carboxyl-ended free radicals that initiate monomer molecules, producing growing macroradicals. These growing macroradicals evidently react with the DTDGA through cleavage of the sulfur—sulfur bond to form a carboxyl-end capped oligomer. This reaction will reduce the probability of chain termination of the growing acrylate radical by combination and disproportionation. A representation of a tentative reaction mechanism is shown in Figure 1. It is evident from the mechanism that the functionality of the oligomer should be 2. However, the functionality of the oligomers is in the range of 1.7–1.9 (Table II). The deviation of calculated functionality from the theoretical value 2 most probably results from some polymer chains being terminated by monomer chain transfer reaction or disproportionation.

It appears from GPC analysis (Table II) that the molecular-weight distributions (\bar{M}_w/\bar{M}_n) are rather large. This might be because of the high reaction rate of bulk polymerization, so that the reaction heat could not be evolved fast enough. Bell et al.¹⁹ have also reported on the high poly-

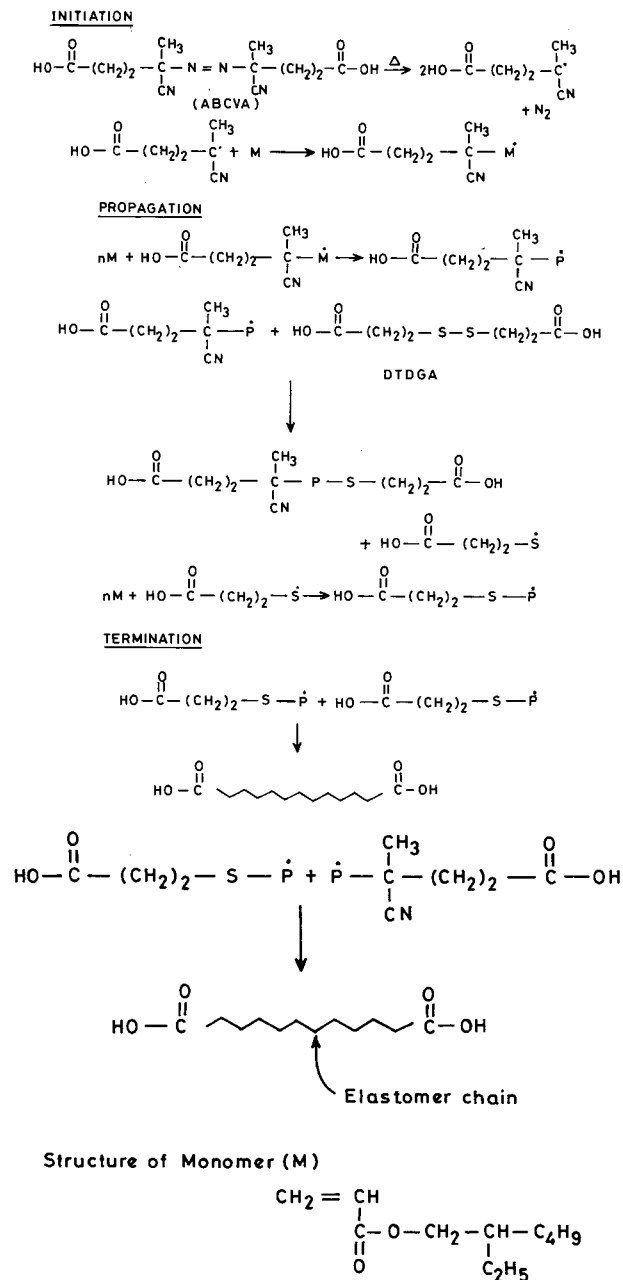
**Figure 1** Tentative Mechanism for polymerization of EHA: ($\dot{\text{P}} = n\dot{\text{M}}$).

Table III Physicochemical Properties of Liquid Rubbers (Synthesized by Solution Polymerization)

Liquid Rubber	Solvent #	\bar{M}_n^a	\bar{M}_n^b	\bar{M}_w^b/\bar{M}_n^b	Carboxyl Content (meq/mol)	Functionality (f) (eq/mol)
LR-5	Dioxan	2360	1900	2.3	0.511	1.2
LR-6	THF	2700	2200	2.7	0.455	1.3

^a Measured by VPO.^b Measured by GPC.

used for synthesis

dispersity index with bulk polymerization of butyl acrylate. By choosing solution polymerization, the heat dissipation problem can be solved. Two liquid rubbers, LR-5 and LR-6, were prepared using solution polymerization in dioxan and in tetrahydrofuran (THF), respectively. Their molecular-weight distributions and functionalities are reported in Table III.

Both the oligomers show narrower molecular-weight distributions in comparison with the oligomers synthesized using bulk polymerization. However, the solution polymerization reduced the functionality, as shown in Table III. The lower functionality ($f = 1.3$) of the oligomers obtained from solution polymerization, in comparison with those obtained from bulk polymerization, most probably results from disproportionation and participation of the solvent in a chain transfer reaction.

Prereaction of Liquid Rubbers with Epoxy and Curing

For effective toughening, the liquid rubber must be chemically bound to the epoxy matrix.^{20,21} Moreover, collection of free liquid-rubber molecules at the metal interface can act as a weak boundary layer in adhesive joints, leading to a substantial decrease in adhesive joint strength.^{22,23} For this reason, before curing the epoxy resin was prereacted with CTPEHA in the presence of TPP as a catalyst until titration showed no carboxyl groups remained. The reaction is basically a carboxyl-epoxide esterification, as proposed by Romanchick et al.²⁴

The product was an epoxy end-capped poly(2-ethylhexyl acrylate)-epoxy copolymer that is capable of reacting with the hardener in the same way as epoxy. A large excess of epoxy resin was used for end-capping the CTPEHA, which made it possible for each carboxyl group to react with an unreacted DGEBA molecule and essentially pre-

vent further polymerization. This reaction is illustrated in Figure 2 (step 1). The changes in viscosity of CTPEHA-modified epoxy because of incorporation of 10 phr (parts per 100 grams of resin) of liquid rubber are listed in Table IV. As expected, the viscosity increases after prereaction from chain extension. All the modified samples are liquid, and no solidification or gelling was observed after the prereaction. The prereacted resin (a mixture of modified and unmodified ep-

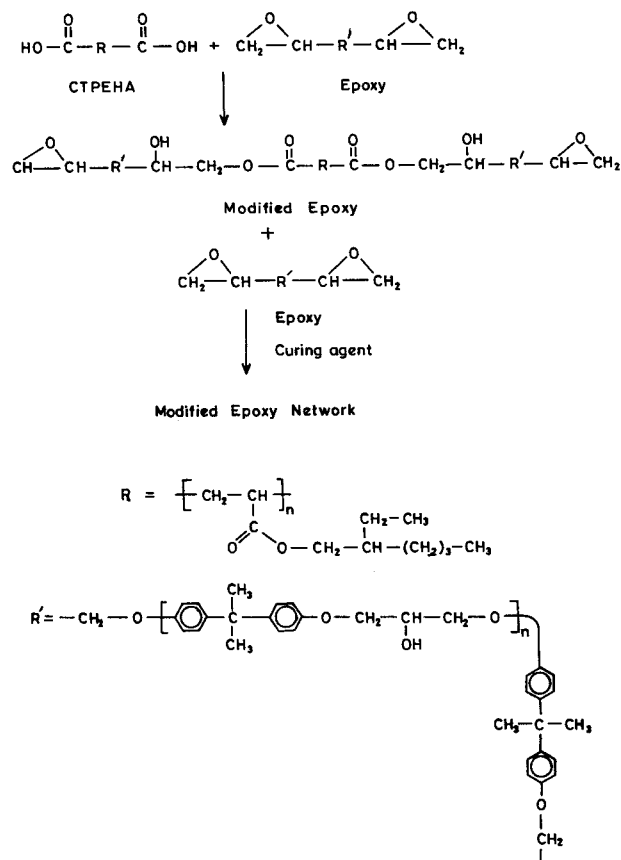
**Figure 2** Prereaction of CTPEHA with epoxy and curing.

Table IV Carboxyl Group Concentration and Viscosity of 10 phr Liquid-Rubber-Modified Epoxy Before and After Precuring

Sample	Carboxyl Content (meq/g)		Viscosity (Pas)	
	Before Precure	After Precure	Before Precure	After Precure
Epoxy/LR-1	0.017	0	15.3	37.4
Epoxy/LR-2	0.022	0	13.2	31.3
Epoxy/LR-3	0.031	0	11.6	26.2
Epoxy/LR-4	0.048	0	10.2	22.4
Epoxy/LR-5	0.046	0	8.3	17.8
Epoxy/LR-6	0.041	0	8.1	17.1

oxy) was then cured with HY 951 or HY 960 to obtain the crosslinked networks (step 2, Fig. 2).

Impact Properties of Modified Networks

To study the effect of molecular weight and functionality of CTPEHA on the fracture properties of modified networks, CTPEHA of different molecular weights and functionalities (LR-1 to LR-6) were prereacted with epoxy resin, and the cured modified networks were evaluated with respect to their impact properties. Figure 3 shows the impact energy of the toughened networks modified with various liquid rubbers. From the figure it is clear that incorporation of liquid rubbers like LR-2, LR-3, and LR-4 resulted in considerable improvement of impact strength with respect to the unmodified epoxy. Approximately a twofold increase in impact strength was achieved. This result is comparable with that reported by Achary et al.⁷ for an ambient-temperature-curing epoxy system using CTBN as the liquid rubber. There is no significant difference in properties when the epoxy is modified with LR-2, LR-3 and LR-4. This indicates that liquid rubbers with a number-average molecular weight in the range of 3500–7000 and a carboxyl functionality in the range of 1.7–1.9 perform almost equally in toughening epoxy resin. However, the liquid rubber LR-1 ($M_w = 9500$, $f = 1.8$) was found to be ineffective in toughening epoxy. This is because of the formation of large agglomerates, as observed in the SEM studies [Fig. 4(b)].

It was also found that incorporation of LR-5 and LR-6 had little effect on the fracture properties of the modified networks. This can be explained by considering the rubber particles to ep-

oxy matrix interfacial adhesion.^{25,26} LR-2, LR-3, and LR-4, because of their bifunctional nature ($f = 1.7$ – 1.9), can form strong chemical bonds with the epoxy matrix and imparts considerable fracture resistance. On the other hand, LR-5 and LR-6 cannot form strong chemical bonds due to their lower functionality ($f = 1.3$). This might be the reason behind the performance difference of LR-5 & LR-6 compared to LR-4. However, the effect of the difference in molecular weight and molecular-weight distribution and compatibility on the fracture properties of modified networks cannot be overruled.

SEM Studies

In order to correlate the molecular and morphological parameters with the fracture properties of the toughened networks, the microstructure of the fracture surfaces of LR-1- and LR-4-modified epoxy networks were analyzed by the SEM. The SEM photographs of the toughened networks containing 10 phr of LR-1 and LR-4 are shown in Figure 4.

It is clear from the photographs that the fracture surfaces of the modified networks consist of two distinct phases: globular rubber particles dispersed in continuous epoxy matrix. In the case of the LR-4 modified epoxy network, the rubber particles are uniformly distributed throughout the matrix. The particles have dimensions in the range of 1–5 μm , and their distribution is bimodal in nature.

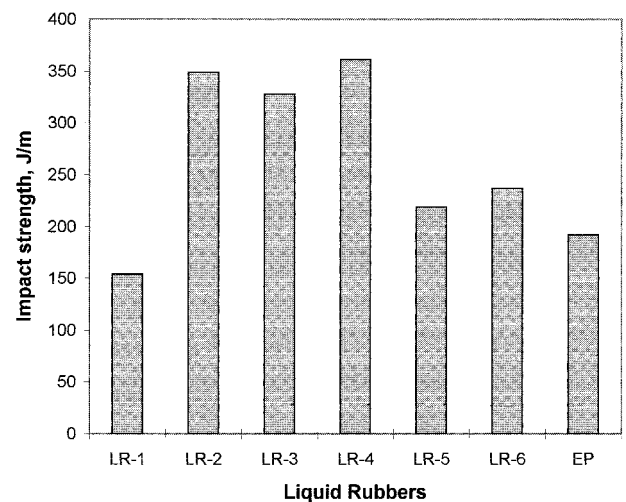
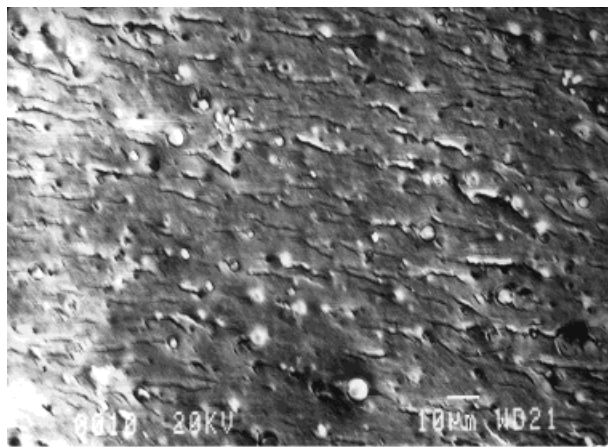
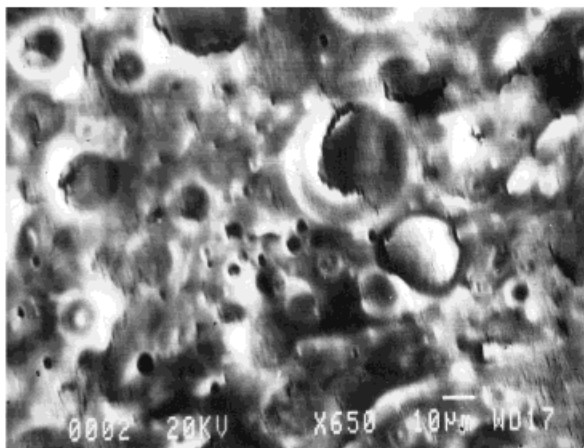


Figure 3 Effect of molecular weight and functionality of CTPEHA on impact strength of modified epoxy networks.



(a)



(b)

Figure 4 SEM microphotographs of fracture surfaces of (a) LR-4 ($\bar{M}_n = 3600$) modified epoxy and (b) LR-1 ($\bar{M}_n = 9500$) modified epoxy network.

The micrograph [Fig. 4(a)] shows the broken rubber particles and a stress-whitened zone. Stress whitening is due to the scattering of visible light from the layer of the scattering centers, which in this case are voids.^{27,28} The voids are generated by the cavitation of rubber particles, which is the most important energy-dissipating mechanism in the case of rubber-toughened epoxy.^{29,30} Uniform distribution of the rubber particles throughout the matrix is very important for toughening, as it allows the yielding process to operate throughout the matrix.^{29–31} This explains why the LR-4-modified ep-

oxy exhibits higher impact strength in comparison to the unmodified epoxy.

The poor fracture property of the LR-1-modified epoxy can also be explained by considering the morphology as observed in the SEM. The SEM photograph indicates the presence of large particles ($> 10 \mu\text{m}$) distributed haphazardly. The larger particles cannot act efficiently in dissipating mechanical energy but instead act as defects^{32,33} and thereby reduce the impact strength.

Effect of Matrix Ductility

The influence of matrix ductility on toughening has also been studied. Two different types of epoxy networks were made using HY 951 and HY 960 as curing agents. The network developed by using HY 960 is more brittle and has lower impact energy as compared to the network made using HY 951. The lower fracture resistance of the LY 556/HY 960 system compared to the LY 556/HY 951 system can be explained in light of the chemical structures of the hardeners (Table I). HY 960 contains a rigid aromatic ring, while HY 951 contains a flexible aliphatic chain. The impact energies of LR-4-modified epoxy networks and unmodified networks are shown in Table V. It is clear from the table that there is greater improvement of fracture energy in the case of the network cured with HY 951, which is more ductile.

The importance of the ductility of the matrix has been reported in the modification of epoxy resins with a liquid rubber such as CTBN.^{34–36} CTBN acts as an effective toughening agent for piperidine-cured epoxy resin but is less effective in the case of an epoxy–DDS system.³⁷ Levita et al.³⁸ have shown that a plot of the fracture energy of the toughened network versus the fracture energy of the unmodified resin shows an amplification factor of 10. This is because the rubber-rich particles act as stress concentrators and induce plastic deformation of a highly brittle matrix to a far lesser extent.

Table V Effect of Matrix Ductility on Toughening of Epoxy Resin Modified with LR-4

Material	Impact Energy (J/m)
Unmodified epoxy ^a	19 ± 3
Modified epoxy ^a	36 ± 4
Unmodified epoxy ^b	10 ± 2
Modified epoxy ^b	15 ± 3

^a Cured by HY 951.

^b Cured by HY 960.

CONCLUSION

The functionality and molecular weight of CT-PEHA had significant influences on the impact strength of the modified epoxy networks. It was found that for effective toughening the molecular weight of the liquid rubber must be less than 7000 and functionality must be greater than 1.7. It was also found that the toughenability of the modified networks increases with an increase in the inherent ductility of the matrix.

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