

Acrylate-Based Liquid Rubber as Impact Modifier for Epoxy Resin

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Received 10 March 2000; accepted 19 July 2000

ABSTRACT: Carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) having various molecular weights were synthesized by bulk polymerization in the form of liquid rubber. The liquid rubbers (LR-1 to LR-4) were characterized by ¹³C-NMR spectroscopic analysis, nonaqueous titration, and vapor-pressure osmometry (VPO). The liquid rubber having the lowest molecular weight ($\bar{M}_n = 3600$) was prereacted 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 CTPEHA were evaluated with respect to their thermal and impact properties. The optimum properties were obtained at about 10–15 phr of CTPEHA concentration (phr stands for parts per hundred parts of epoxy resin). Fracture surface analysis by scanning electron microscopy (SEM) indicated the presence of a two-phase microstructure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1792–1801, 2001

Key words: epoxy; 2-ethyl hexyl acrylate; impact, modified epoxy

INTRODUCTION

Epoxy resins are a class of versatile thermosetting polymers, which are widely used as structural adhesives, composites, surface coatings, and electrical laminates,¹ because of their high strength, low creep, very low cure shrinkage, and excellent resistance to corrosion, good adhesion to many substrates, and appropriate electrical properties.² However, the major drawback of epoxy resins is that in the cured state they are brittle materials having a fracture energy of about two orders of magnitude lower than engineering thermoplastics and three orders lower than metals.³ This inherent brittleness causes poor damage tolerance to impact of the composites made from epoxy resin and 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 Sultan and McGarry⁴ 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.^{5–7} The theory is that liquid rubber reacts with the epoxy through the carboxylic functional groups. During initial stage, the reactive liquid rubber is compatible with the epoxy-hardener mixture. As the curing reaction proceeds, the molecular weight increases and phase separation occurs at a some stage, leading to the formation of a two-phase morphology. The improvement in fracture toughness is achieved without a significant reduction of 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

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Journal of Applied Polymer Science, Vol. 80, 1792–1801 (2001)
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Table I Physicochemical Properties of Liquid Rubbers

Liquid Rubber CTPEHA	DTDGA Concentration (mol %)	(\bar{M}_n)	Carboxyl Content (meq/g)	Functionality (<i>f</i>) equiv/mol	Viscosity (Pa s)
LR-1	2	9500	0.19	1.8	69.4
LR-2	5	7000	0.25	1.7	54.7
LR-3	8	5300	0.34	1.8	36.9
LR-4	10	3600	0.52	1.9	27.5

not suitable for use at high temperature.⁸ One would imagine that excessive crosslinking could take place with time which would detract from otherwise desirable improvements accomplished with these structures. Second, there is some limitation in its use due to the possibility of the presence of traces of free acrylonitrile, which is carcinogenic.⁹ Moreover, most of the reported rubber-toughened epoxy formulations suffer from the problem of 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 coatings and adhesives onto the intricate structure. Acrylate-based liquid rubber may be an ideal choice for toughening epoxy resin because of its comparatively better oxidative and thermal stability.¹⁰

The aim of the present work was to develop a low molecular weight liquid carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) and to examine its effect as an impact modifier for epoxy resin. The present article discusses the synthesis and characterization of CTPEHA, the development of CTPEHA-modified epoxy networks using an ambient temperature curing agent, and their evaluation with respect to their thermal and impact properties.

EXPERIMENTAL

Materials

The monomer 2-ethyl hexyl acrylate (EHA; Fluka, Buchs, Switzerland) was purified by washing twice with a sodium hydroxide solution (5% w/v) to remove the inhibitors and then washed repeatedly with distilled water. It was then dried over anhydrous calcium chloride for 48 h. 4,4'-Azobis(4-cyanovaleric acid) (ABCVA; Aldrich, Milwaukee, WI) was recrystallized from ethanol before using it as a free-radical initiator. Dithiodiglycolic acid (DTDGA;

Aldrich) was used as a chain-transfer agent without further purification. Triphenylphosphine (TPP; SISCO, Mumbai, India) was used as received. Solvents like toluene and methanol were of analytical grade (BDH, Mumbai, India).

The epoxy resin was a liquid diglycidyl ether of bisphenol A (Ciba Geigy, Basel, Switzerland, Araldite LY 556) with an equivalent weight per epoxide group of 195 ± 5 . An ambient temperature hardener, triethylene tetramine (TETA; Ciba Geigy, HY 951), was used as the curing agent.

Synthesis and Characterization of CTPEHA

CTPEHA liquid rubbers, having various molecular weights, were synthesized by bulk polymerization, using ABCVA as a free-radical initiator and DTDGA as a chain-transfer agent. 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 the 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. The unreacted monomer and solvent were removed under a vacuum on a rotary evaporator until a constant weight was obtained.

¹³C-NMR spectra were recorded on 500-MHz FTNMR instrument (Bruker AMX-500) using chloroform as a solvent and tetramethylsilane as an internal standard. 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

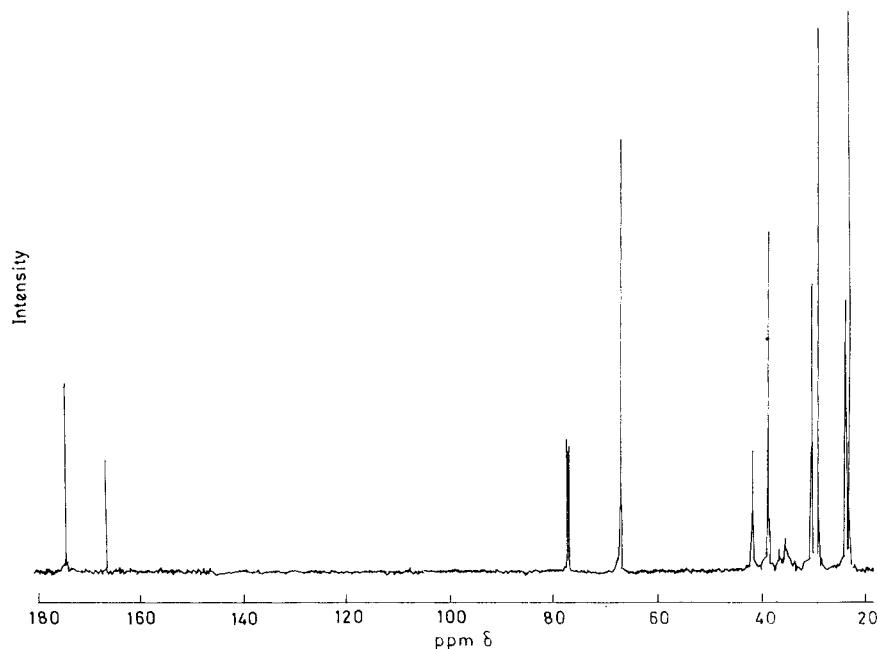


Figure 1 ^{13}C -NMR spectrum of CTPEHA.

(Haake RVIII) at a shear rate range of $0\text{--}100\text{ s}^{-1}$ 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 weight (\bar{M}_n) of CTPEHA was determined with a Knauer vapor-pressure osmometer (VPO) using toluene as the solvent and benzil as a standard. The functionality (f) of the oligomer was calculated by multiplying the carboxyl content, expressed in equiv/g with the number-average molecular weight. The functionality was expressed as equiv/mol.

Modification of Epoxy and Curing

CTPEHA, having the lowest molecular weight (100 g , 0.027 mol), was prereacted with the epoxy resin (100 g , 0.53 mol) using TPP (1 g) as the catalyst. The reaction was carried out at 80°C under a nitrogen atmosphere until all the carboxyl groups were completely reacted. The epoxy end-capped poly(2-ethyl hexyl acrylate) oligomer was then diluted with an appropriate amount of epoxy resin to obtain various concentrations of CTPEHA in the formulations.

All the formulations were analyzed for their epoxy content by standard titration with hydrogen bromide in acetic acid. Accordingly, a stoichiometric amount (26 g for 1 equivalent of epoxy) of TETA was added and thoroughly mixed. The mix-

ture was cast into a Teflon mold and cured at room temperature (RT) for 2 days. The samples were postcured at 80°C for 2 h.

Characterization of Modified Epoxy Networks

A DSC instrument (DuPont 910) was used for the curing study and determination of the glass transition temperature (T_g). A heating rate of $10^\circ\text{C}/\text{min}$, sample weight of about 20 mg , and a nitrogen flow of $60\text{ mL}/\text{min}$ were maintained for all the experiments.

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

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 the cases were $125 \times 10 \times 4\text{ mm}^3$. 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 samples which are not notched.

A low-voltage scanning electron microscope (SEM; JEOL, JSM- 840) was used to examine the

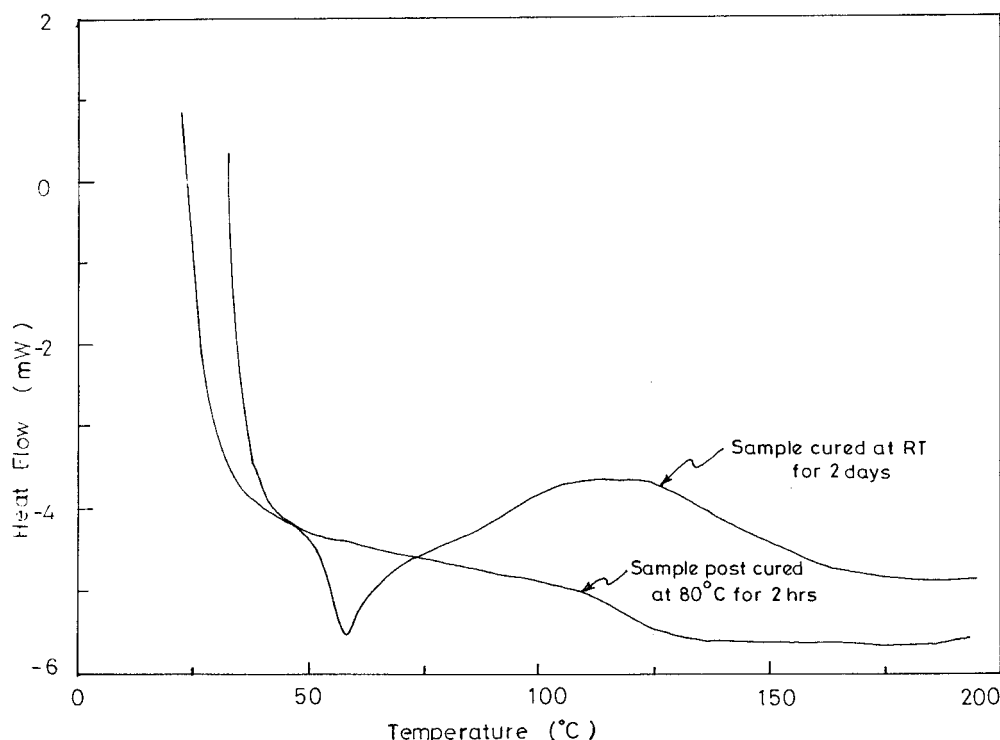


Figure 3 DSC trace of 10 phr CTPEHA-modified epoxy before and after postcuring.

weight. The functionality of the liquid rubbers are in the range of 1.7–1.9, which indicates essentially their telechelic nature.

The ^{13}C -NMR spectrum for CTPEHA is shown in Figure 1. The NMR spectrum clearly shows two peaks for carboxyl and ester carbon. The peaks at 174–174.4 and 166 ppm can be attributed to the presence of the ester and carboxylic acid carbon, respectively. The higher intensity of the ester peak can be explained due to that the carboxyl groups are present only in the terminal position, whereas every repeat unit of the oligomer has an ester group. The peak at 77 ppm is due to the

solvent CDCl_3 . The peaks at 41 and 36 ppm are due to the carbon atom attached to $-\text{O}$ and the $-\text{C}=\text{O}$ group, respectively. The rest of the peaks at 30–10 ppm are for aliphatic carbon atoms.

Prereaction of CTPEHA with Epoxy and Curing

For effective toughening, the liquid rubber is required to be chemically bonded to the epoxy matrix.^{11,12} 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 the adhesive joint strength.¹³ For this reason, before curing, the epoxy resin was prereacted with CTPEHA (having the lowest molecular weight) in the presence of TPP as the catalyst until titration showed that no carboxyl group remained. The reaction is basically a carboxyl–epoxide esterification.

The product obtained was an epoxy end-capped poly(2-ethyl hexyl acrylate)–epoxy copolymer which is capable of reacting with the hardener in the same way as does epoxy. A large excess of the 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 prevented further polymer-

Table II Glass Transition Temperature of CTPEHA-Modified Epoxy

Epoxy/CTPEHA Composition	Glass Transition Temperature (°C)
100/0	115
100/5	115
100/10	113
100/15	108
100/20	104
100/30	95

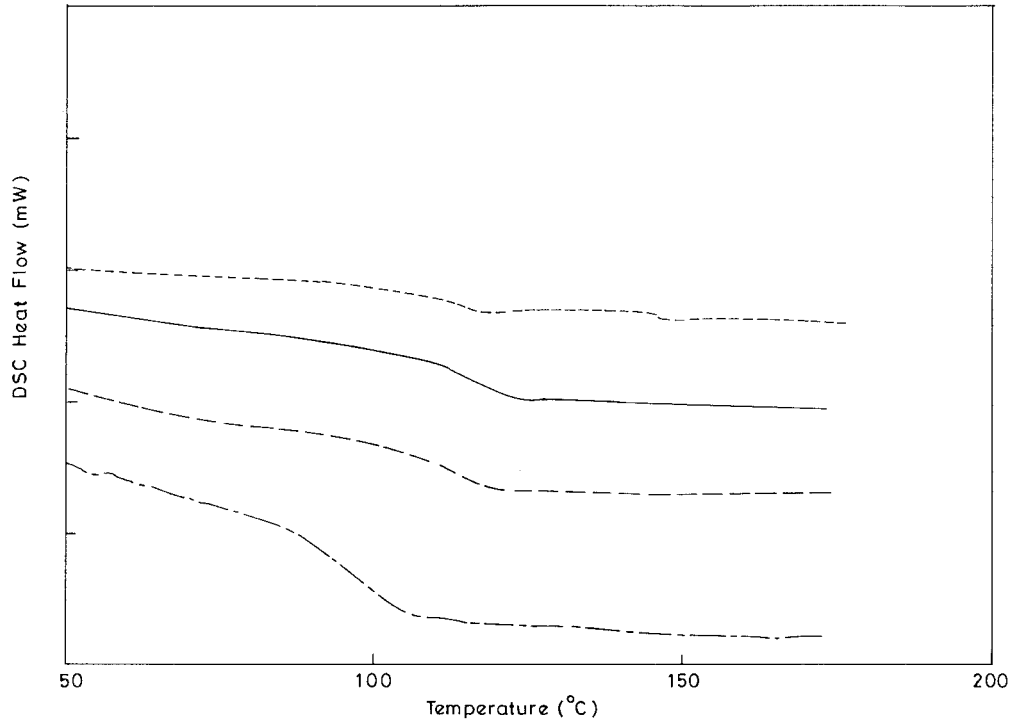


Figure 4 DSC scan of postcured CTPEHA-modified epoxy networks: (—) 0 phr; (---) 10 phr; (- -) 20 phr; (- · -) 30 phr.

ization. The reaction is illustrated in Figure 2 (step 1). The modified sample is liquid and no solidification or gelling was observed after pre-reaction. The diluted resin was then cured with HY 951 to obtain the crosslinked networks (step 2, Fig. 2).

Characterization of Modified Networks

The modified networks containing different concentrations (0–30 phr) of CTPEHA ($\bar{M}_n = 3600$) were evaluated for their thermal and impact properties in order to study the effect of the modifier concentration on the properties of the modified networks. The correlation of molecular weights of the liquid rubbers and the properties of the modified networks will be discussed in a separate communication.

Thermal Analysis

The modified epoxy network containing 10 phr of CTPEHA was subjected to DSC analysis after curing for 2 days at room temperature. The DSC trace is shown in Figure 3. It shows a residual exotherm and glass transition region at a low-temperature range (50–60°C). The same sample when postcured at 80°C for 2 h shows no residual

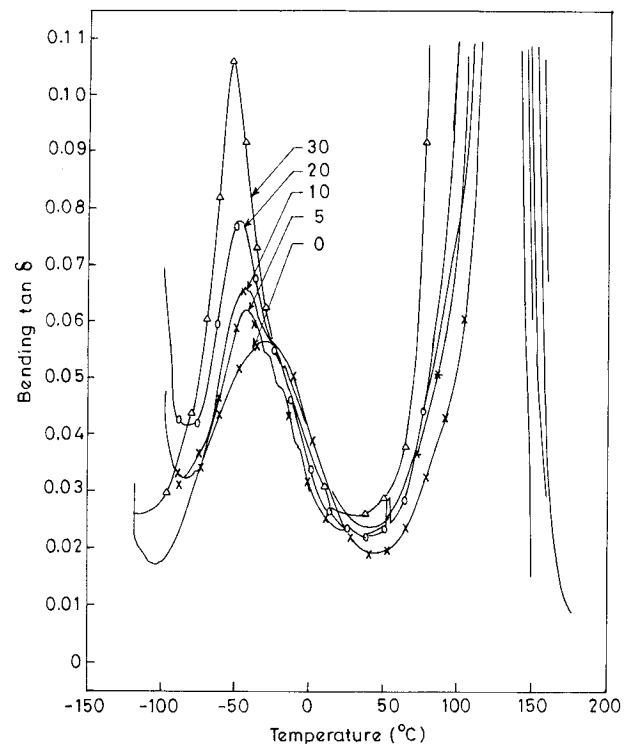


Figure 5 Low-temperature transitions of CTPEHA-modified epoxy with 0, 5, 10, 20, and 30 phr of CTPEHA.

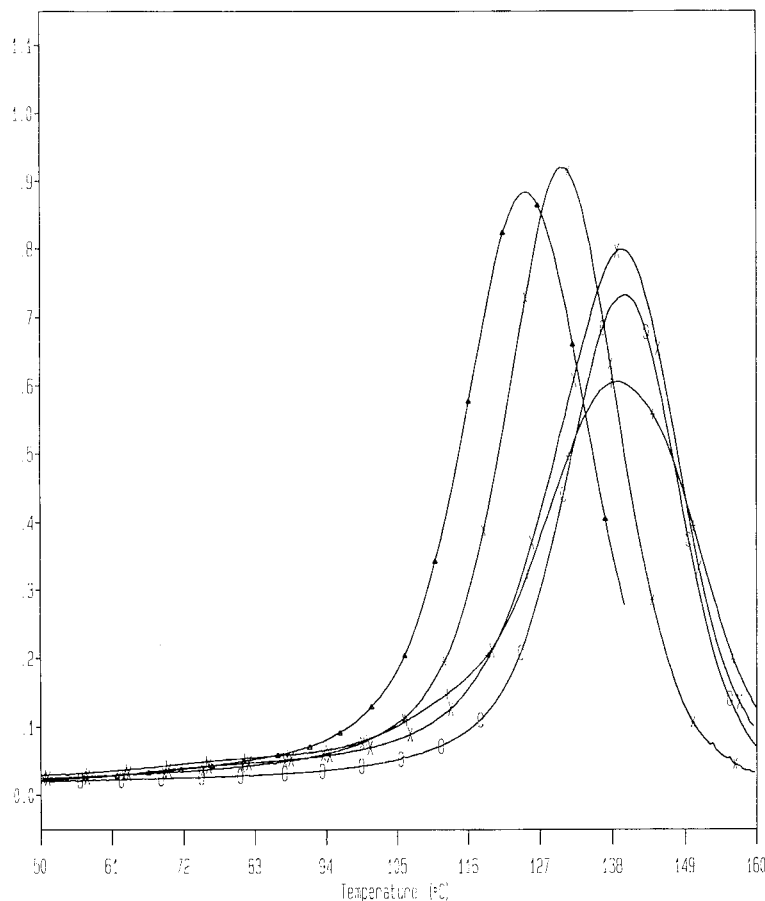


Figure 6 High-temperature transition of CTPEHA-modified epoxy networks: (+--+-) 0 phr; (-o-o-) 5 phr; (-x-x-) 10 phr; (-*-*-) 20 phr; (-▲-▲-) 30 phr.

exotherm and the T_g was shifted to 115°C, which indicates further crosslinking at an elevated temperature. The heat evolved during the curing reaction is often used to estimate the reaction rate and conversion. Although the residual heat of reaction near the completion of curing cannot be measured by DSC, the amount of heat evolved as

measured by DSC is still a valuable reference in the determination of curing characteristics.¹⁴ The absence of any residual exotherm in the post-cured-modified epoxy sample as seen in Figure 3 confirms the completion of the curing reaction. Therefore, the T_g of all the samples were determined after postcuring.

The experimental T_g values obtained from DSC for all the modified networks containing different concentrations of CTPEHA are listed in Table II. Some of the representative curves are shown in Figure 4. From the table, it is clear that up to 10 phr of CTPEHA there is no change in the T_g of the cured epoxy resin and a slight reduction in T_g was observed at higher concentrations. This indirectly implies that there is phase separation. The slight reduction in T_g in the cases of the modified networks having higher concentrations of CTPEHA (20, 30 phr) can be attributed to the dissolution of a certain amount of rubber in the epoxy matrix. The amount of dissolved rubber

Table III DMTA Analysis of CTPEHA-modified Epoxy Networks

Concentration of CTPEHA (phr)	Storage Modulus ^a (GPa)	Tan δ Peak Temperature (°C)	Tan δ_{\max}
0	2.69	140	0.60
5	2.32	139	0.73
10	2.04	139	0.80
20	1.78	130	0.92
30	1.49	125	0.88

^a At 35°C.

increases with increase in the concentration of the added rubber, causing more and more reduction of the epoxy T_g . A slight reduction of the epoxy T_g was also reported by others¹⁵ using CTBN as the liquid rubber.

The rubber T_g is not discernible in DSC. However, it is detected clearly by DMA, which is related to the mechanical relaxation. The advantage of DMA over many other methods in the determination of the T_g is that it is sensitive enough to detect even weak transitions. In fact, all the properties measured by this technique generate strong well-defined signals that are not clouded by background noise or other interference.

The pure epoxy and CTPEHA-modified epoxy samples were subjected to DMA analysis from -100 to 150°C . All the modified networks show two transition peaks. The effects of CTPEHA concentration on low-temperature and high-temperature relaxation peaks are shown in Figures 5 and 6, which represent the loss factor ($\tan \delta$) plots against temperature for pure and CTPEHA-modified epoxy networks. From the figures, it is clear that all the modified networks show two relaxation peaks: One at -40°C and other at 140°C . The former peak is attributed to the α relaxation of CTPEHA and the latter peak is due to α relaxation of the unmodified epoxy. The height of the low-temperature relaxation peak gradually increases with the incorporation of CTPEHA. This indicates that there is phase separation, resulting in an epoxy phase and a CTPEHA-rich epoxy phase. Lee et al.¹⁶ reported a similar observation for a CTBN-modified epoxy system.

From the dynamic spectra, the values of the storage moduli (E') at 35°C , $\tan \delta_{\text{max}}$ (maximum $\tan \delta$ value), and the $\tan \delta$ peak temperature (α relaxation temperature) were obtained and are summarized in Table III. From the table, it is evident that up to 10 phr of CTPEHA concentration there is little change in the $\tan \delta$ peak temperature but a decrease of the same was observed for the modified networks having a higher concentration of CTPEHA. This supports the DSC results. The difference between the exact temperature for the glass transition (T_g) from DSC and from DMA is about 20°C . It is expected due to the difference in the method of measurement and a different definition of the transition temperature used. The storage modulus decreases with the incorporation of CTPEHA. This can be attributed to the presence of a low-modulus rubber.¹⁵

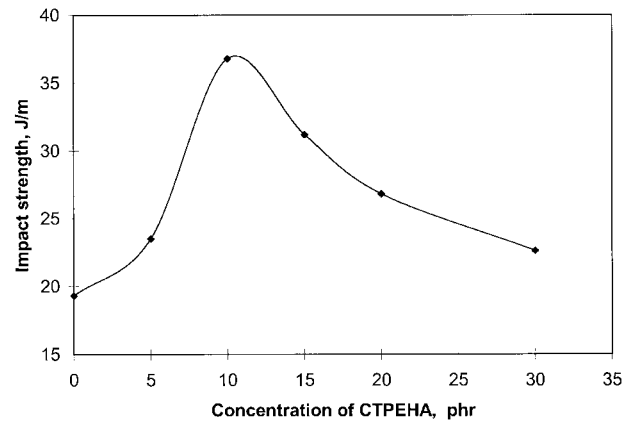


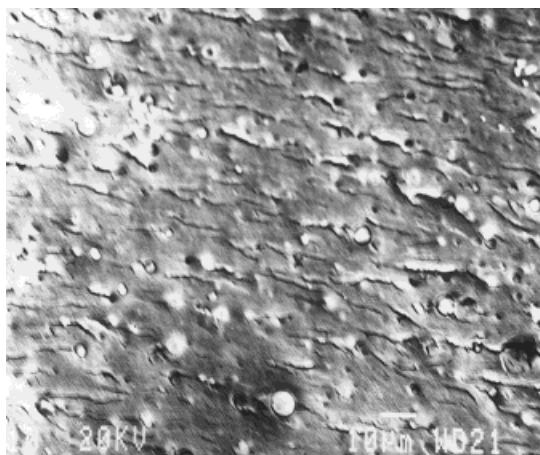
Figure 7 Effect of CTPEHA concentration on the impact strength of the modified epoxy networks.

Impact Properties

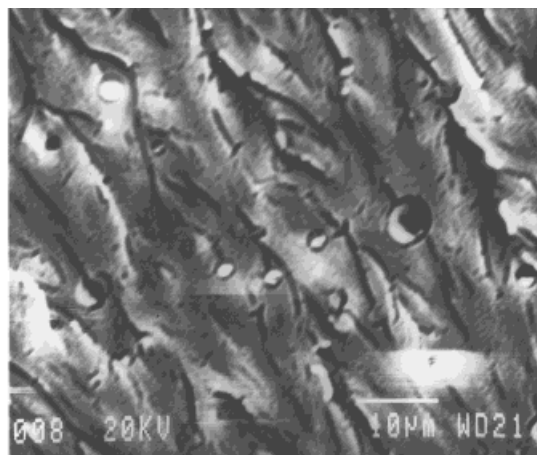
The effect of CTPEHA concentration on the impact properties of the modified networks is shown in Figure 7. It is clear from the figure that the improvement of the impact strength was achieved as a result of the addition of CTPEHA. The impact energy gradually increases with increase in the CTPEHA concentration, attains a maximum, and then again decreases. The maximum impact strength (36 J/m) was obtained at 10–15 phr of CTPEHA concentration. Approximately a twofold increase in the impact strength was achieved. This result is comparable with that reported by Achary et al.⁶ for an ambient temperature curing epoxy system using CTBN as the liquid rubber. It is well established that small rubber particles dispersed in the epoxy matrix increases the impact resistance by cavitation and shear yielding.¹⁷ The reduction of the impact energy after an optimum concentration is due to the breakdown of the desired particulate morphology. This will be discussed in the SEM studies.

SEM Analysis

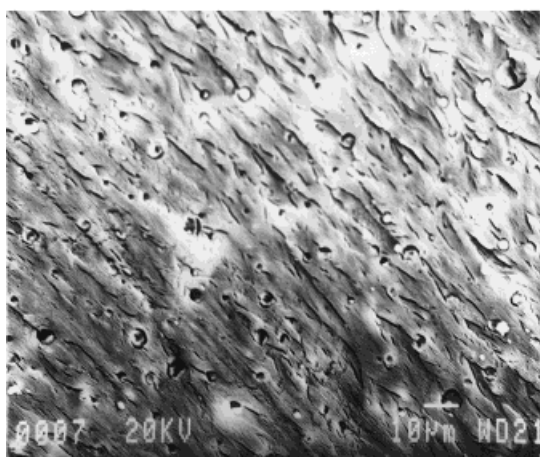
To correlate the molecular and morphological parameters with the fracture properties of the toughened networks, the microstructure of the fracture surfaces of various CTPEHA-modified networks were analyzed by SEM. SEM photographs for the toughened networks containing different concentrations of CTPEHA are shown in Figure 8. It is clear from the photographs that the fracture surfaces of the modified networks consist of two distinct phases: Globular rubber particles are dispersed in a continuous epoxy matrix. In the case of the modified epoxy network having 10 phr



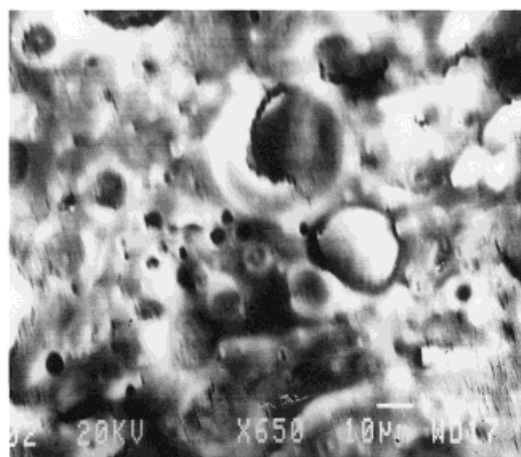
(a)



(b)



(c)



(d)

Figure 8 SEM photographs for the fracture surfaces of CTPEHA-modified epoxy networks: (a) 10 phr; (b) same as (a) at higher magnification; (c) 20 phr; (d) 30 phr.

of CTPEHA, the rubber particles are uniformly distributed throughout the matrix. The particles' size is in the range of 1–5 μm and the distribution of particles is bimodal in nature.

In the photographs [Fig. 8(a,b)], one can see the broken rubber particles and the stress-whitened zone. Stress whitening is due to the scattering of visible light from the layer of the scattering cen-

ter—in this case, voids.¹⁸ The generation of the voids is due to the cavitation of rubber particles, which is the most important energy-dissipating mechanism in the case of rubber-toughened epoxy. The matrix surrounding the voids exhibits notable plastic deformation as evidenced by the bevelled edge of the voids. It clearly supports the crack-terminating mechanism.

Uniform distribution of the rubber particles in the matrix is very important as it allows the yielding process to operate throughout the matrix.^{18,19} In the case of the modified networks having a higher concentration of CTPEHA, the uniform morphology is disturbed due to agglomeration, as evident from the photographs [Fig. 8(c,d)]. The presence of agglomerates acts as defects and initiates catastrophic failure. This explains why the impact property attains a maximum value at about 10–15 phr and decreases subsequently.

CONCLUSIONS

A low molecular weight carboxyl-terminated poly(2-ethyl hexyl acrylate) liquid rubber was developed. The liquid rubber is completely compatible with epoxy after prereaction but generates a two-phase microstructure on curing with a room-temperature hardener. It can be used as a toughening agent for epoxy resin.

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