Phase separation in liquid rubber modified epoxy mixture. Relationship between curing conditions, morphology and ultimate behavior

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Abstract

Chemorheology of curing as well as the phase separation behavior of carboxyl-terminated poly(2-ethyl hexyl acylate) (CTPEHA) liquid rubber-modified epoxy mixtures have been studied by several techniques. The CTPEHA was incorporated into the epoxy matrix by a prereact method. The delay in polymerization for the modified mixtures with respect to that of the neat resin can be explained by lower reactivity of the chain extended resin and viscosity effect. The phase separation has been proved for various rubber contents and as a function of cure conditions used as well. The thermal and dynamic viscoelastic behavior of the modified matrices have been examined and compared to the unmodified epoxy matrix. Finally, flexural and impact properties have been discussed in terms of the morphological behavior for an epoxy matrix modified with various amounts of CTPEHA and for a 10 phr (phr stands for parts per hundred parts of epoxy resin) CTPEHA containing matrix cured at different temperatures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid rubber; Modified epoxy; Phase separation

1. Introduction

One of the most successful methods to toughen epoxy resin is the incorporation of rubbery phase into the brittle epoxy matrix. This is achieved by the use of reactive liquid rubber [1] or preformed rubber particles [2]. An attraction of liquid rubber as a modifier is their solubility in the base epoxy initially with the formation of a homogeneous solution. As the curing reaction proceeds, the molecular weight increases and the phase separation occurs at some stage, leading to the formation of a two-phase morphology [3]. Extensive studies [4–7] have shown that the phase separation process is a result of the decrease in configurational entropy due to the increase in molecular weight as epoxy cures. This changes the free energy of mixing leading to a decrease in solubility of the rubber that provides the driving force for phase separation. Various morphological parameters like particle size, particle size distribution, interparticle distance, matrix to particle adhesion, play an important role in toughening [8–10]. These morphological parameters depend on chemistry, molecular weight and

concentration of the liquid rubber [10,11] as well as on the curing condition [12].

Most of the studies reported in the literature have used carboxyl-terminated copolymer of acrylonitrile and butadiene, CTBN. However, the main deficiency of CTBN is the high level of unsaturation in their structure, which provides sites for degradation reaction in oxidative and high temperature environment [13]. The presence of double bonds in the chain can cause oxidation reaction and/or further cross-linking with the loss of elastomeric properties and ductility of the precipitated particles [14]. Secondly, there remains a possibility that traces of free acrylonitrile, which is carcinogenic, might exist and limit the use of these materials [15]. In contrast to CTBN liquid rubber, modifiers based on functionalized acrylic oligomers do not contain unsaturated bonds in the backbone, resulting in good resistance against oxidation process [16–18]. Previous publications of the author [19,20] have shown that carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubbers ($\bar{M}_n = 3600$–7000, $f = 1.7$–1.9) can be used as an impact modifier for epoxy resin cured with an ambient temperature hardener.

The aim of the present work is to examine its suitability as a toughening agent in case of high temperature curing system and to study the effect of initial cure temperature

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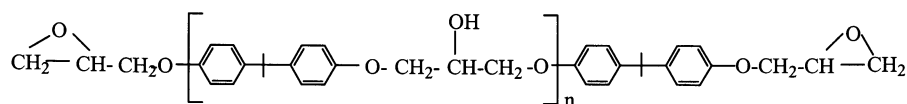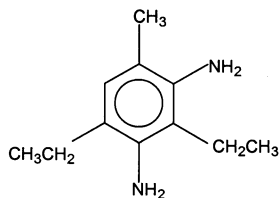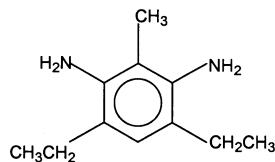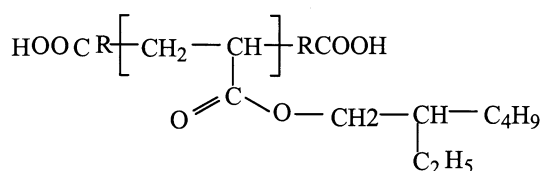 *E-mail address:* ratna@ncml.ernet.in (D. Ratna).

Fig. 1. Chemical structure of epoxy resin, curing agent and liquid rubbers.

on the morphology and final properties of the modified networks. The paper discusses thermal and impact behavior and morphology of the rubber toughened epoxy networks.

2. Experimental

2.1. Materials

The epoxy resin used was a liquid diglycidyl ether of bisphenol A (DGEBA) (Ciba Geigy, Araldite LY 556) with an equivalent weight per epoxide group of 195 ± 5. The curing agent, Ethacure 100, of Albemarle Corporation is a mixture of the two diethyltoluene diamine (DETD) isomers (74–80% 2,4 isomer and 18–24% 2,6 isomer).

The liquid rubber, carboxyl terminated CTPEHA ($\bar{M}_n = 3600$, $f = 1.9$) was synthesized by bulk polymerization as discussed elsewhere [19].

The CTBN was the product of B.F. Goodrich Products, 'Hycar', carboxyl-terminated acrylonitrile–butadiene liquid elastomer, type X-13 containing 27% acrylonitrile.

The chemical structures of the epoxy resin, hardener, CTBN and CTPEHA liquid rubbers are shown in Fig. 1.

2.2. Prereaction of liquid rubber with epoxy and curing

CTPEHA (100 pbw) (pbw stands for parts by weight) was prereacted with epoxy resin (100 pbw) using tri-phenyl phosphine (1 pbw) as a catalyst. The reaction was carried out at 100°C under nitrogen atmosphere until all the carboxyl groups were completely reacted. The reaction mixture 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 [21] with hydrogen bromide in acetic acid and accordingly a stoichiometric amount (23:100 w/w) of DETD was added by continuously stirring the mixture for 5 min. The mixtures were cured in an aluminum mold at 100°C for 3 h after having degassed under vacuum for 10 min. In order to study the effect of cure temperature on the properties modified networks, the 10 phr liquid rubber containing mixture was cured at different
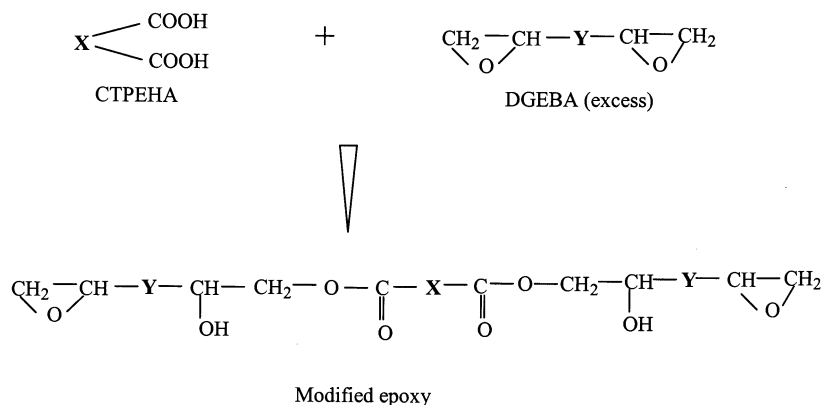
Fig. 2. Prereaction of epoxy resin with CTPEHA.

temperatures (120, 140, 160, 180°C). Hence curing temperature means 100°C unless specified. Afterwards, the samples were post cured at 200°C for 2 h, allowing them to cool gradually to room temperature.

Differential scanning calorimeter (DSC) dynamic mode measurements were carried out with a Perkin–Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an Indium standard) working with 8–10 mg samples in aluminum pans. Runs at constant heating rate of 10°C min^{-1}, were performed in a temperature range 50–300°C for every mixture. The heat evolved during the reaction of the mixture has been directly determined by integration of the exothermic peaks. The glass transition temperature, T_g was taken in a second scan as the beginning point of the endothermic shift in the DSC scan. T_g of the samples cured using the cure schedule were also determined by the same instrument using liquid nitrogen for sub-ambient region.

A Bohlin CS 10 controlled stress rheometer was used to study the variation in rheological properties during cure. A parallel plate assembly (40 mm diameter) was used in the oscillatory mode at a constant frequency of 1 Hz while applying a constant shear stress of 300 Pa. Gelation was defined as the point where the loss factor (tan δ) becomes independent of frequency [22]. The point where the loss tangent vs. time plots at various frequencies (1, 2.1, 4.4, 9.4, 20 and 42.9 Hz), intersect each other is taken as gel point. The viscosity of the modified resins were also determined from the same instrument.

2.3. Characterization of modified epoxy networks

Dynamic mechanical analysis (DMA) were carried out for cured epoxy samples by a Dynamic Mechanical Thermal Analyzer (DMTA MK IV, Rheometric Scientific) at a fixed frequency of 1 Hz with 3°C/min heating rate using liquid nitrogen for sub-ambient region. Dynamic modulii and loss

factors were obtained by dual cantilever mode for the sample of size $45 \times 10 \times 2$ mm^3.

The flexural properties were measured with rectangular samples according to ASTM D-790, using the same UTM at a crosshead speed of 2 mm/min. The sample size was $120 \times 25 \times 2.5$ mm^3. The flexural strength (FS) was determined from the following formula:

$$FS = 3/2 \times \text{Peak Load} \times \text{Span} \times 9.8/\text{width} \times (\text{thickness})^2 \tag{1}$$

The results are expressed in MegaPascals, which is the average of the results from three samples. The flexural strain was determined by an LVDT system.

The Izod impact test was carried out according to ASTM D-256 using an impact tester (Tinius Olsen, Model 892 T). The impact test was carried out at room temperature and the impact energy was reported in Joules per meter. The quoted result is the average of the determinations on six samples.

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. SEM microphotographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

3. Results and discussion

For effective toughening, the liquid rubber must be chemically bound to the epoxy matrix [23,24]. 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
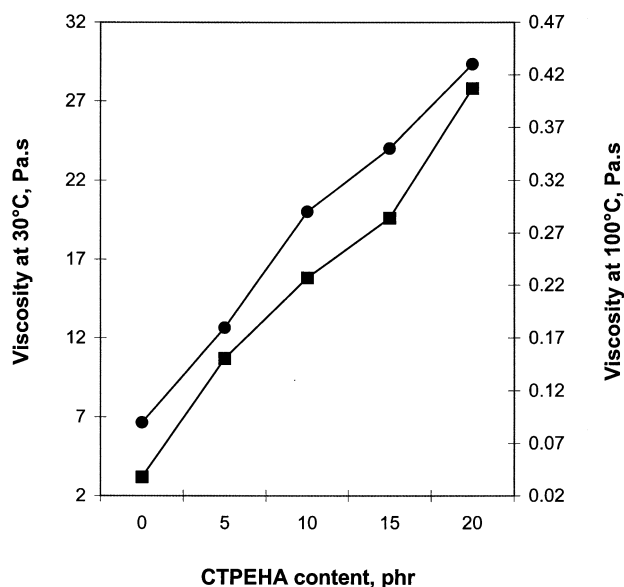
Fig. 3. Effect of rubber loading on viscosity of modified network at 30 (—■—) and at 100°C (—●—).

Fig. 4. Effect of rubber modification on gel time of modified resins at 100°C.

[25]. For this reason before curing the epoxy resin was prereacted with CTPEHA in the presence of TPP as a catalyst until titration showed that no carboxyl groups remained. The reaction is basically a carboxyl-epoxide esterification, as proposed by Romanchick et al. [26].

The product 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 epoxy. A large excess of epoxy resin was used for end capping CTPEHA, which made it possible for each carboxyl group to react with an unreacted DGEBA molecule and essentially prevents further polymerization. The reaction is illustrated in Fig. 2. All the modified samples are liquid and no solidification or gelling was observed after the prereaction. Fig. 3 shows the viscosity (at 30 and 100°C) of prereacted epoxy resin containing various concentrations of CTPEHA. There is significant increase in viscosity as a result of modification.

Rheological measurement carried out in a parallel plate viscometer at 100°C permitted the characterization of gelation and vitrification processes during curing. The effect of liquid rubber concentration on the gel time is shown in Fig. 4. It is clear from the figure that the gel time increases with the increase in the rubber concentration. This delay can be attributed to lower reactivity of the modified epoxy produced as a result of chain extension and increase in viscosity of the medium due to the addition of rubber as shown in Fig. 3. The delay in cure kinetics was confirmed by thermal measurement carried out at $10°C \, min^{-1}$. As shown in Fig. 5, the temperature corresponding to exothermic peak, T_{peak} gradually increases with increase in the CTPEHA content. However, when CTPEHA is blended directly without prereaction, the T_{peak} was found to appear at lower temperature compared to neat epoxy. This indicates the accelerating effect of CTPEHA carboxyl groups on the
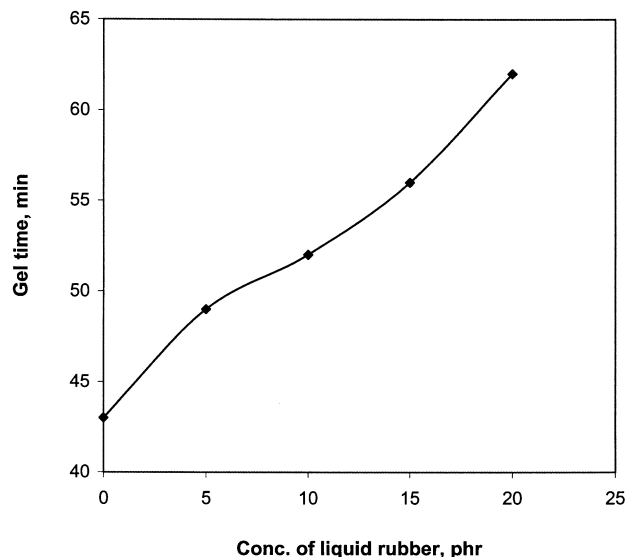
cure of DGEBA/DETD. This behavior can be interpreted in terms of intermolecular transition state for epoxy–amine reaction — according to this mechanism [27,28], strong hydrogen-bonding species, such as acids and alcohols stabilizes the transition state and strongly accelerates the reaction. The accelerating effect in rubber modified epoxy system is also reported using CTBN [29]. As expected, total enthalpy as shown in Fig. 6, decreased proportionately to the rubber amount in the mixture. The ΔH_p of unfilled epoxy/DETDA was found to be 101 J mol^{-1} (expressed in terms of mass of epoxide/ amine mixture) which compares with 91.4 J mol^{-1} found by Barton [30] for DGEBA/ Diaminodiphenyl methane system and values ranging from 100–118 J mol^{-1} for phenyl glycidyl ether type epoxy-amine reactions tabulated in a review by Rozenberg [31].

After curing in a DSC cell up to 300°C, each sample was allowed to cool down to room temperature and subjected to a second run. From the DSC trace, obtained in the second run, the T_g was determined. The modified networks cured using the cure schedule mentioned in the experimental, were also analyzed by DSC from −100 to 250°C. The results were reported in Table 1. All the modified networks exhibit two glass transition temperatures indicating phase separation. The depression of epoxy T_g can be attributed to the presence of some amount of dissolved rubber which is observed in varied rubber modified formulations [9,17,22]. The amount of dissolved rubber increases with an increase in the concentration of added rubber causing more and more depression of epoxy T_g. Up to 10 phr of CTPEHA concentration there is only a slight decrease in epoxy T_g indicating almost completion of phase separation. In case of room temperature curing system, CTPEHA modification does not cause any depression of epoxy T_g [19,20]. This is the advantage of these materials over the
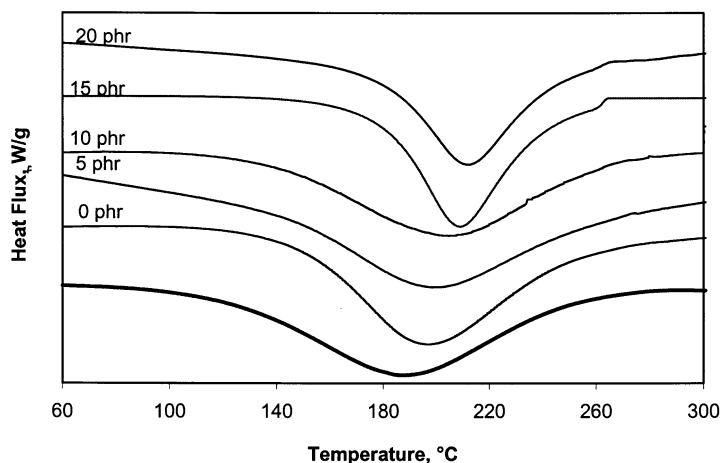
Fig. 5. DSC scan of (━) 100/10 DGEBA/CTPEHA blend without preparation and (—) preacted DGEBA resin containing 0, 5, 10, 15, 20 phr of CTPEHA.

other liquid rubber modified epoxy resin where significant depression of epoxy T_g due to incomplete phase separation was observed.

The clearly lower T_gs observed for dynamically scanned rubber modified mixture with respect to those polymerized with the cure schedule, outlines the importance of control of cure temperature. Thus, the difference shown in T_g values quoted in Table 1 for the mixtures cured by the above-referred ways would be connected to distinct levels of segregation through phase separation during the dynamic curing, and during polymerization with the cure schedule. In the case of dynamic scan the rubber does not get sufficient time to undergo phase separation completely.

Since CTPEHA forms chemical bonds with the epoxy resin, the T_g of the precipitated rubber is expected to be higher than pure CTPEHA. However, it is observed that the T_g of CTPEHA when precipitated from the epoxy matrix is $-60°C$, which is lower than the T_g of CTPEHA when it is in its pure form ($-45°C$). A similar result was reported in CTBN [29] and epoxidized soybean oil modified epoxy

systems [32]. This can be explained by considering thermal shrinkage stresses [4,29,32]. Triaxial thermal shrinkage stress develops in the dispersed domain phase on cooling through epoxy glass transition temperature since the coefficient of thermal expansion of the rubbery state is larger than that of the glassy state. This triaxial stress increases the free volume of the rubber particles and depresses the T_g of the precipitated rubbery phase.

The effect of cure temperature on the T_g of the modified networks containing 10 phr of CTPEHA, is shown in Fig. 7. The T_g of the modified networks decreases with increase in cure temperature. This indicates that as the cure temperature increases the amount of rubber which remains dissolved in the epoxy matrix increases. The samples cured at 180°C is almost transparent indicating little phase separation. This can be explained by considering the fact that phase separation proceeds until complete gelation, when diffusion of modifier molecules within the continuous matrix phase is inhibited [33]. From the onset of phase separation, the structure evolves up to gelation at which particle dimension and interparticle distances are fixed. As the curing temperature is increased, the times available for particle nucleation and growth becomes considerably shorter partly because the compatibility is increased and phase separation is initiated at higher conversion.

Fig. 8 shows DMTA data for pure epoxy and 10 and 20 phr CTPEHA modified epoxy. The modified networks shows two relaxation peaks: one at ca. 215°C for epoxy and other at ca. $-50°C$ which can be assigned to the glass transition of rubber. This supports the DSC results. The pure epoxy also shows a broad peak at low temperature which is often attributed to crankshaft motion of the glyceryl-like groups in DGEBA [34]. The shift of relaxation peak towards low temperature as a result of modification can be attributed to the presence of dissolved rubber. The shoulders in the loss tangent vs. temperature curves in case of unmodified and 10 phr CTPEHA modified networks indicates presence of region of lower crosslink density as the post cure
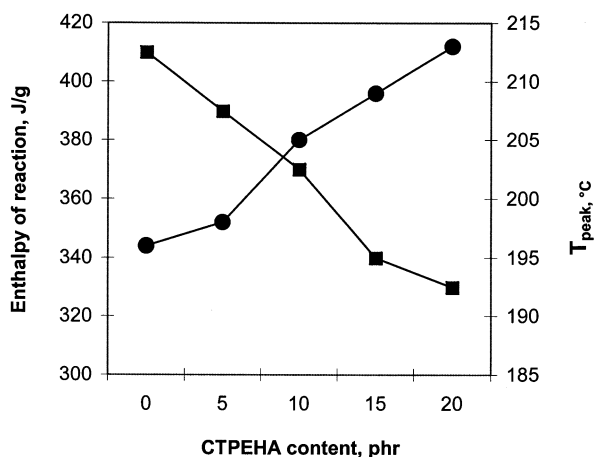

Fig. 6. Effect CTPEHA loading on enthalpy (—■—) and T_{peak} (—●—).

Table 1
Thermal properties of CTPEHA-modified epoxy mixtures

DGEBA/CTPEHA	100/0	100/5	100/10	100/15	100/20	0/100
T_g (°C)[a]	203	198, −60	196, −60	185, −55	174, −58	−45
T_g^b (°C)	200	190	178	170	160	–

[a] Values determimined from DSC analysis (−100 to 300°C) of the cured networks, polymerized using cure schedule.

[b] Values correspond to second run (25–300°C) after a dynamic scan up to 300°C.

temperature (200°C) was lower than the loss tangent peak temperature.

The flexural properties of the modified networks were shown in Fig. 9. The flexural strength and modulus of the modified epoxy networks are lower than that of the unmodified epoxy. The decrease in modulus can be attributed to the presence of low modulus rubber particles into the epoxy matrix. The reduction in flexural strength is due to the
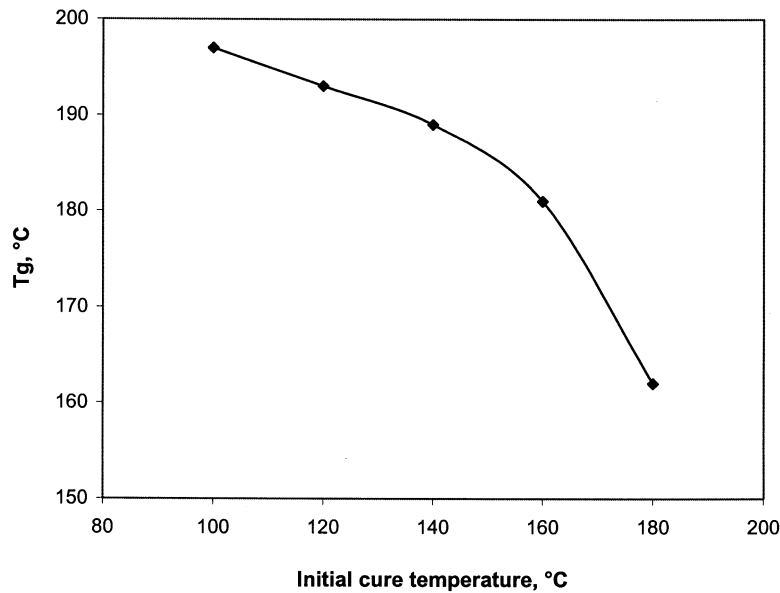

Fig. 7. Effect of cure temperature on T_g of modified networks.
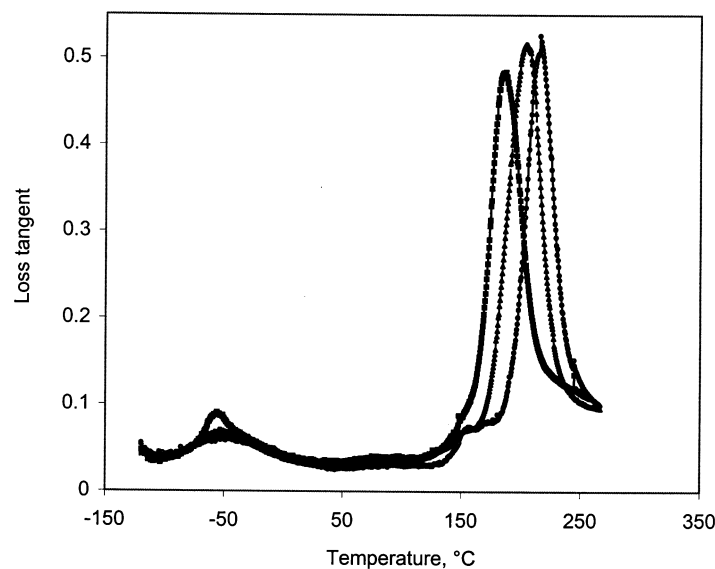

Fig. 8. DMTA plots of unmodified epoxy (—●—), 10 phr (—▲—) and 20 phr (—■—) CTPEHA modified epoxy.
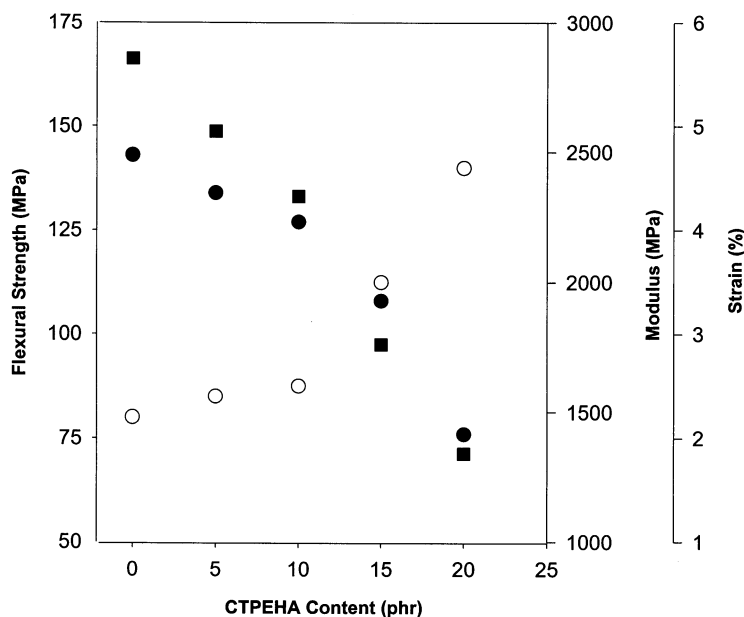
Fig. 9. Flexural properties of CTPEHA modified epoxy networks: Flexural strength (●), Modulus (■) and strain (○).

presence of some amount of rubber, which remains dissolved in the epoxy matrix as evident from the reduction in T_g values (Table 1). Similar observations have been reported by many authors using various liquid rubbers [17–19,35]. However, this is in direct contradiction to the observation made by Achary et al. where they have reported an increase in the tensile strength as a result of the incorporation of CTBN and carboxyl-terminated poly(propylene glycol) adipate liquid rubber. Up to 10 phr of CTPEHA, only a modest decrease in modulus was observed. A more significant reduction was observed in case of modified networks containing 15 and 20 phr CTPEHA. This indicates a plasticizing effect of the dissolved rubber as is also evident from the decrease in T_g. The plasticizing effect is also reflected in the significant increase in flexural strain in case of 15 and 20 phr CTPEHA modified epoxy networks.

The relationship between the concentration of CTPEHA and notched Izod impact strength per unit width of the specimen is shown in Fig. 10. The impact strength of the modified epoxy samples is higher than that of the unmodified epoxy and its value passes through a maximum as the concentration of CTPEHA increases. The modified network containing 10 phr rubber shows maximum impact strength of 25.6 J/m which is about 60% higher than that for the neat epoxy (16.3 J/m). The impact strength is marginally higher than the value (24.9 J/m) observed for the same epoxy system containing 10 phr CTBN. However, the improvement in impact strength is less compared to that observed in case of a more ductile DGEBA/triethylene tetramine matrix containing 10 phr of the same liquid rubber, reported earlier [19]. The importance of ductility of the matrix has been reported in the modification of epoxy resin with liquid
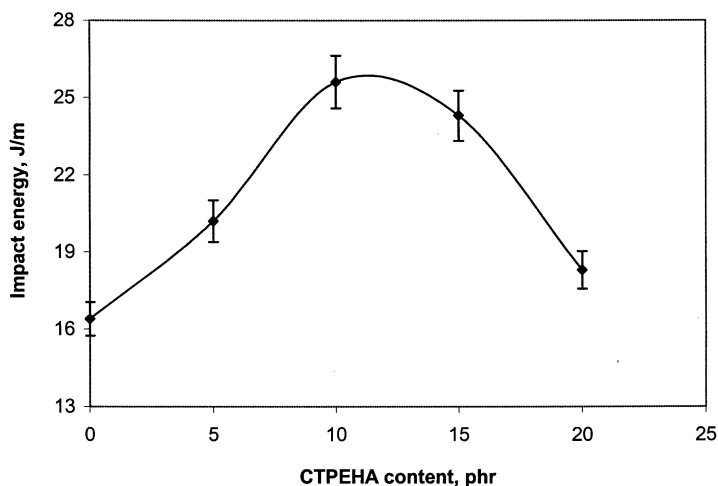

Fig. 10. Effect of concentration of liquid rubber on the impact strength of modified epoxy networks.
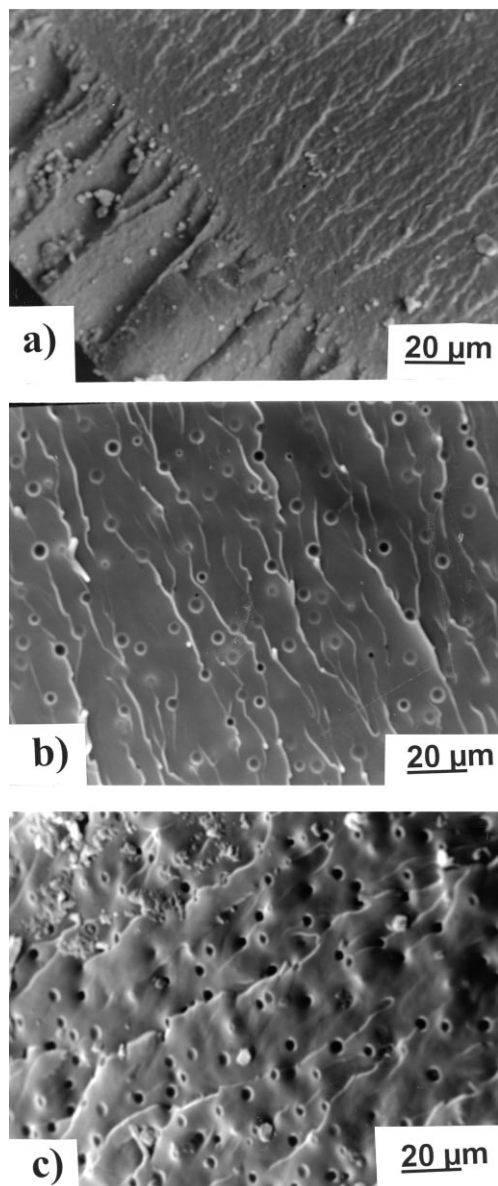
Fig. 11. SEM photo micrographs for the fracture surfaces of modified epoxy having CTPEHA concentrations: (a) 0; (b) 10; and (c) 20 phr.

Fig. 12. Effect of cure temperature on the impact strength of modified epoxy networks.

rubber like CTBN [36,37]. CTBN acts as an effective toughening agent for piperidine cured epoxy resin, but is less effective in the case of an epoxy/diamino diphenyl sulfone (DDS) system [38]. Levita et al. [39] have shown that a plot of the fracture energy of the toughened network vs. 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.

The impact behavior of the modified epoxy networks can be explained in terms of the morphology observed by SEM. The SEM microphotographs for unmodified epoxy and 10 and 20 phr CTPEHA modified epoxy mixtures are shown in Fig. 11. From the photograph (Fig. 11a) one can see the smooth glassy fractured surface with cracks in different
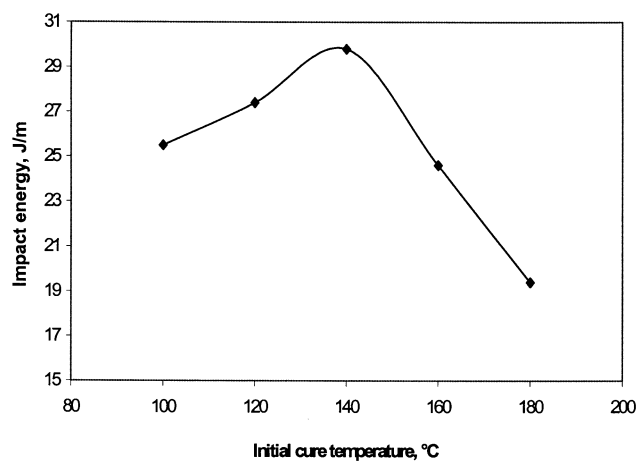
planes in the case of the unmodified epoxy. This indicates a brittle fracture of the unmodified epoxy, which accounts for its poor impact strength. The fracture surfaces of the modified networks consist of two distinct phases: globular rubber particles dispersed in continuous epoxy matrix. In the case of 10 phr rubber modified sample the rubber particles are uniformly distributed throughout the matrix. The particles have dimensions in the range of 1–3 μm and their distribution is bimodal in nature. The micrograph (Fig. 11b) 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 [40,41]. 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 [42,43]. 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 [42–44]. This explains why the rubber modified epoxy exhibits higher impact strength in comparison to the unmodified epoxy. In the case of mixtures having higher rubber content, the uniform morphology is disturbed due to agglomeration (Fig. 11c) leading to the reduction in fracture toughness.

The effect of initial cure temperature on the impact strength of the modified networks containing 10 phr rubber is also investigated. As shown in Fig. 12, the impact strength of the modified networks slowly increases with increase in cure temperature up to 140°C and decreases with further increase in cure temperature. The sample cured at 180°C shows significantly lower toughness. The impact behavior can be explained in terms of the morphology observed by SEM. The morphology of the mixtures cured at 140 and 180°C are shown in Fig. 13. The small size of the discrete particles with unimodal distribution increased with an increase in the curing temperature. This seems to indicate that phase separation started in the gelation region, so the particle growth was not possible because of the diffusional
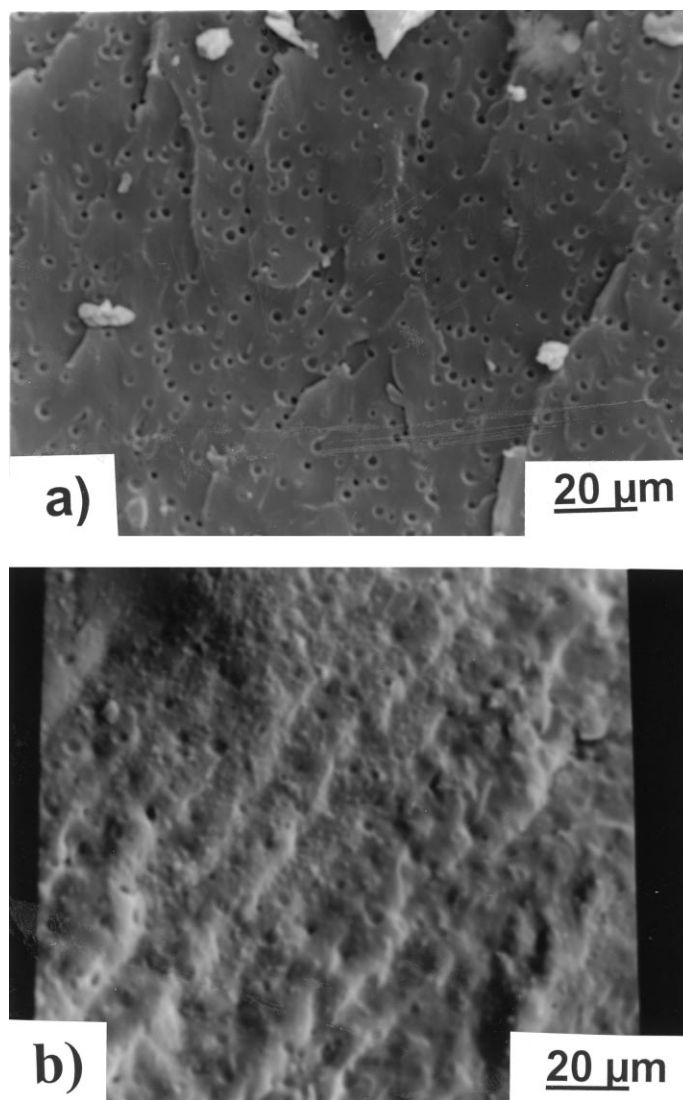
Fig. 13. SEM photographs for the fracture surfaces of 10 phr CTPEHA modified epoxy: (a) cured at 140°C and (b) cured at 180°C.

restriction exiting after gelation of the epoxy matrix. A similar observation was reported by Kim et al. [45] in the case of CTBN modified epoxy and Moller et al. [46] in the case of thermoplastic toughened epoxy.

However, the rubber particles of the observed size are reported to perform equally [47]. Hence, the increase in toughness due to an increase in cure temperature can be explained in terms of dissolved rubber. As evident from the DSC analysis the amount of dissolved rubber increases with an increase in cure temperature. The dissolved rubber makes the matrix more ductile and increases its toughness [36–39]. The fracture surface of the sample cured at 180°C shows almost single phase morphology with little phase separated rubber which explains it poor impact performance, as it is well known nowadays that phase separation is a boundary condition for toughening in rubber modified system. Unlike the unmodified epoxy, fracture surface is rough indicating massive shear deformation. Energy is absorbed during plastic deformation in case of the modified

epoxy network giving rise to a higher toughness and impact strength [48]. Thus the modified network cured at 180°C shows higher impact strength compared to the unmodified epoxy. However, the improvement in impact strength is less in a system where epoxy and rubber phases have been rendered miscible and no phase separated rubber exists.

4. Conclusions

Addition of CTPEHA liquid rubber causes a delay in polymerization of the epoxy matrix. This delay can be attributed to the chain extension during prereaction and viscosity effect. The T_g of the epoxy matrix decreases with increase in rubber concentration and cure temperature. The T_g of the rubbery CTPEHA phase was also lower than the T_g of the neat CTPEHA. The cause of this depression of T_g has not been determined although the possible reason was discussed.

The importance of the control of initial cure temperature on the final morphology and impact property of the modified mixtures have been proved. Thus for the 10 phr CTPEHA containing mixtures complete transparency and trans-lucidity can be obtained as a function of cure temperature. Optimum impact performance was achieved for the mixture containing 10 phr of CTPEHA and cured at 140°C, which contains both phase-separated rubber as well as dissolved rubber.

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