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Polymer 42 (2001) 7739–7747

polymer

www.elsevier.nl/locate/polymer

Mechanical characterization and morphology of carboxyl randomized poly(2-ethyl hexyl acrylate) liquid rubber toughened epoxy resins

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Received 8 May 2000; accepted 11 December 2000

Abstract

A family of carboxyl randomized poly(2-ethyl hexyl acrylate) (CRPEHA) liquid rubbers which are 2-ethyl hexyl acrylate–acrylic acid copolymers (LR-1 to LR-4) with different carboxyl functionality were synthesized. The liquid rubbers were characterized by nonaqueous titration, vapor pressure osmometry (VPO) and solubility characteristics. All the liquid rubbers were reacted with the epoxy resin in 10:100 weight ratio using tri-phenyl phosphene (TPP) as a catalyst. The modified epoxy networks were made by reacting the homogeneous, prereacted resin with an ambient temperature curing agent. The effects of functionality of the liquid rubbers and ductility of the matrix, on the mechanical properties of the modified networks were investigated. The results were explained in terms of morphology observed by SEM. There is an optimum functionality which leads to best impact performance. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy; 2-Ethyl hexyl acrylate; Impact

1. Introduction

Epoxy resins are a class of versatile thermosetting polymers, which are widely used, in structural adhesives, composites, surface coatings and electrical laminates [1]. This is because of their high strength, low creep, very low cure shrinkage, excellent resistance to corrosion, good adhesion to many substrates and appropriate electrical properties [1,2]. A major drawback, which inhibits further proliferation of epoxy resins into various industrial applications, is that in the cured state they are brittle materials having fracture energy of about two orders of magnitude lower than engineering thermoplastics and three orders lower than metals [3]. Hence, modification of epoxy resin to impart fracture toughness has been the subject of intense investigation throughout the world.

Toughness implies energy absorption and achieved through various deformation mechanisms before failure occurs and during crack propagation [4]. Toughening can be achieved by reduction of crosslink density or use of plasticizers, which lead to increased plastic deformation. However, this approach may seriously affect modulus and thermal properties of the material for only modest increase in toughness. The most effective approach is the introduction of a second component which is capable of phase separation such as reactive liquid rubber [5,6], engineering thermoplastic [7,8] or core-shell particles [9,10]. An attraction of liquid rubber like carboxyl terminated copolymer of butadiene and acrylonitrile (CTBN) as a modifier, is their solubility in base epoxy with the formation of initially 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 [11,12]. Such a two-phase system having a small amount of rubber (10–15 wt%) often shows outstanding fracture properties as the rubber particles dispersed and bonded to the epoxy matrix act as centers for dissipation of mechanical energy by cavitation and shear yielding [6,12]. The improvement in fracture toughness is generally achieved without a significant reduction of thermal and mechanical properties of the crosslinked epoxy resin.

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 crosslinking 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].

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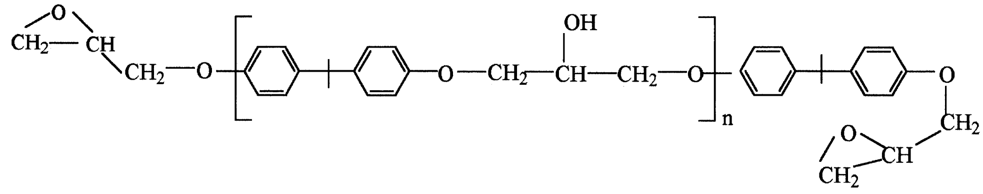
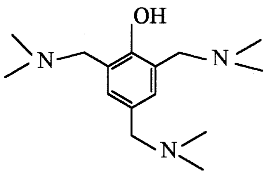
PII: S0032-3861(01)00278-6

Table 1
Chemical structures of epoxy resin and hardeners

Epoxy resin LY 556	
HY 951	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$ Triethylene tetramine (TETA)
HY 960	 Tris (N, N'- dimethyl aminomethyl) phenol

The saturated liquid rubbers such as siloxane [16], polyurethane [17], acrylates [18], etc. have been reported as an alternative to CTBN. Recently, Ratna et al. [19,20] have shown that carboxyl terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubber ($\bar{M}_n = 3600, f = 1.9$) can be used as an effective impact modifier for epoxy resin cured with ambient temperature hardeners. Ambient curing saves energy and is advantageous for surface coating applications and adhesives to the intricate structures. However, the carboxyl terminated acrylate oligomers can only be synthesized by bulk polymerization which is difficult to control. Solution polymerization gives practically monofunctional oligomer, which is ineffective in toughening epoxy resin [20,21].

In the present work, a family of carboxyl randomized poly(2-ethyl hexyl acrylate) (CRPEHA) synthesized by solution polymerization has been used as the toughening agents for epoxy resin. The present paper discusses the mechanical properties and morphology of the toughened networks.

2. Experimental

2.1. Materials

The monomer 2-ethyl hexyl acrylate (EHA) (Fluka) was purified by washing twice with sodium hydroxide solution (5%, w/v) to remove the inhibitors and then repeatedly washed with distilled water. It was then dried over anhydrous calcium chloride for 48 h. Acrylic acid (AA) was obtained from Fluka and was used without further purification. Benzoyl peroxide (BPO) (BDH, India) was repeatedly recrystallized from chloroform prior to using as a free radical initiator and was stored at −25°C. Thioglycolic acid (TGA) (Aldrich) was used as a chain transfer agent without further purification. Triphenyl phosphine (TPP) (SISCO, India) was used as received. Solvents like toluene, dioxan, methanol, etc. were of analytical grade (BDH, India).

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. 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. The ambient temperature hardeners used were an aliphatic polyamine (Ciba Geigy, HY 951) and an aromatic amine (Ciba Geigy, HY 960). The chemical structures of the epoxy resin and hardeners are given in Table 1.

2.2. Synthesis and characterization of CRPEHA

CRPEHA liquid rubbers were synthesized by solution polymerization using dioxan as the solvent, BPO as a free radical initiator and TGA as a chain transfer agent. A typical recipe was inhibitor-free EHA and AA monomer mixture (100 g, 0.54 mol), dioxan (150 ml), BPO (250 mg, 0.001 mol) and TGA (4 g, 0.04 mol). The materials were introduced into a reaction flask (500 ml) fitted with a condenser and a gas inlet. Nitrogen gas was slowly bubbled through for 15 min to remove the dissolved oxygen. The mixture was heated to reflux temperature and allowed to reflux for 5 h. The flask was then allowed to cool and the solvent and the unreacted monomer were removed in a rotary evaporator. The product was then washed with distilled water and treated with anhydrous calcium chloride obtain the dry CRPEHA.

The carboxyl content of CRPEHA was determined by titration with methanolic solution of 0.10N KOH using phenolphthalein as an indicator.

Molecular weights of CRPEHA oligomers were determined using a Knauer vapor pressure osmometer (VPO) using toluene as the solvent and benzil as a standard. The functionality (*f*) of the oligomers was calculated by multiplying the carboxyl content, expressed in equiv./g with the number average molecular weight. The functionality was expressed as equiv./mol.

Solubility parameters were determined by iterative method from the three-dimensional solubility parameters of the solvents in which the polymer is miscible [22,23].

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.

2.3. Modification and curing procedure of epoxy using CRPEHA

Before curing, the epoxy resin was reacted with CRPEHA using TPP as catalyst. Epoxy (100 g), CRPEHA (10 g) and TPP (0.2 g) were added into a three-necked reaction flask blanketed with nitrogen. The flask containing the reaction mixture was placed in an oil bath at 80°C and allowed to react under stirring condition. Every 15 min a small amount of mixture was taken out for carboxyl content analysis. The reaction was continued until no carboxyl group was detected by titration. The reaction time was about 3 h. The modified networks were made by curing all the formulation with HY 951. In order to study the effect of matrix ductility on toughening, an unmodified epoxy network and a modified epoxy network (using the liquid rubber having optimum functionality) were made using HY 960 as curing agent. Hence, unless mentioned curing agent means HY 951.

All the formulations were analyzed for their epoxy content by standard titration [24] with hydrogen bromide in acetic acid, accordingly a stoichiometric amount (26 g for HY 951 or 12 g HY 960 per equivalent of epoxy) of curing agent 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 100°C for 2 h.

Gel times for the unmodified epoxy and modified epoxy of various liquid rubbers were determined as per ASTM D 3532-76. The time when the resin ceases to form strings by contact with a pick is taken as the gel point.

2.4. Characterization of modified networks

2.4.1. Tensile test

Tensile tests were performed on dumb-bell shaped type IV samples according to ASTM D-638. The dumb-bell shaped samples were cut from the molded sheet. The ultimate tensile strength and % elongation at break were measured using a Universal Testing Machine (UTM), Hounsfield H-50 KS. The crosshead speed was 10 mm/min and the gauge length was 45 mm. The elongation at break was measured using a contact extensometer. The results are expressed in MPa, this being calculated by dividing the load (in N) at break by the cross-sectional area of the dumb-bell centerpiece. The quoted result is the average of the results from five dumb-bells.

2.4.2. Flexural test

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 mm × 25 mm × 2.5 mm. The fracture strength was determined from the following formula:

$$\mathrm{FS} = \frac{3}{2} \times \text{peak load} \times \text{span} \times \frac{9.8}{\text{width}} \times (\text{thickness})^2 \qquad (1)$$

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

2.4.3. Impact properties

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 RT and impact energy was reported in J/m. The quoted result is the average of the determinations on six samples.

2.4.4. DSC analysis

Differential scanning calorimetry (DSC) instrument (DuPont 910) was used for determination of glass transition temperature (T_g). A heating rate of 10°C/min, sample weight of about 20 mg and a nitrogen flow of 60 ml/min were maintained for all the experiments. Runs were performed in a temperature range 30–200°C. The T_g value was calculated automatically by the interactive DSC program, picking the inflection point of the break in the heat flow curve.

2.4.5. SEM analysis

A low voltage scanning electron microscope (SEM), (Cameca, SU-30) 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 photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

3. Results and discussion

3.1. Characterization of CRPEHA

The low molecular weight liquid rubbers were

Table 2
Physico-chemical properties of CRPEHA

Liquid rubber	Concentration of AA (wt%)[a]	Molecular weight (g/mol)	Carboxyl content (mmol/g)	Functionality, *f* (equiv./mol)	Solubility parameter $(J/cm^3)^{0.5}$
LR-1	4	2500	0.48	1.2	19.8
LR-2	8	2600	0.69	1.8	20.2
LR-3	12	2500	1.10	2.5	20.4
LR-4	16	2700	1.62	4.4	21.1

[a] With respect to total amount of monomer concentration of TGA = 3 wt%.

synthesized by solution polymerization using varying concentrations of AA as described earlier. The physico-chemical properties of the liquid rubbers are shown in Table 2. All four liquid rubbers have almost same molecular weight (2500–2700 g/mol). However, the carboxyl functionality of the liquid rubber increases from 1.2 to 4.4 equiv./mol with increasing concentration of AA in the feed ratio [25]. The solubility parameter of the liquid rubber also increases with increase in the functionality due to greater polarity of the molecules (Table 2).

3.2. Synthesis of modified epoxy and curing

For an effective toughening, the liquid rubber is required to be chemically bonded to the epoxy matrix [26,27]. Moreover, the collection of free liquid rubber molecules at the metal interface can act as a weak boundary layer in the adhesive joints leading to a substantial decrease in adhesive joint strength [28,29]. For this reason, before curing, the epoxy resin was prereacted with all the liquid rubbers in the ratio of 100:10 (by weight) using TPP as catalyst until titration showed no carboxyl group remained. The reaction is basically *carboxyl*-epoxide esterification, as outlined by Romanchick et al. [30].

The product was an epoxy functionalized poly(2-ethyl hexyl acrylate)–epoxy copolymer, which is capable of reacting with the hardener in the same way as the base epoxy. A large excess of epoxy resin was used for prereaction with CRPEHA which made it possible for each carboxyl group to react with an unreacted DGEBA molecule and essentially prevent further polymerization. The reaction is illustrated in Fig. 1. The change in viscosity of CRPEHA modified epoxy due to incorporation of liquid rubber is listed in Table 3. As expected, the viscosity increases after prereaction due to chain extension. All the modified samples are liquid and no solidification or gelling was observed after the prereaction. When the liquid rubbers having high functionality ($f = 4.4$) and still higher molecular weight ($\bar{M}_n > 2700$) are used, solidification occurs during prereaction. Hence, such liquid rubbers cannot be used effectively as a toughening agent for epoxy resin [31]. Thus, in order to compare the performance of the liquid rubbers with various functionality, the molecular weight range is selected in such a way so that no solidification occurs during prereaction. The effect of molecular weight of the liquid rubber with optimum functionality on toughening will be presented in a latter communication.

The modified resins were then cured with HY 951. The gel times of the unmodified epoxy and modified epoxy samples, with hardener HY 951 at 27°C, are reported in Table 4. The gel times of the modified epoxies are longer than that of the unmodified epoxy. This indicates that the epoxy–CRPEHA copolymer formed as a result of chain extension crosslinks at a slower rate in comparison to the unmodified epoxy. The delay in gelling can also be attributed to the increase in viscosity as a result of chain extension during prereaction (Table 3).

3.3. Glass transition temperature data

The effect of functionality of the liquid rubber on the T_g of the modified networks is shown in Fig. 2. The values of T_g for all the rubber modified epoxy samples are lower than that for the neat system ($T_g = 388$ K). The decrease in T_g for cured rubber modified epoxy systems arises from the incomplete phase separation caused by plasticization phenomenon that has been noted in varied rubber modified

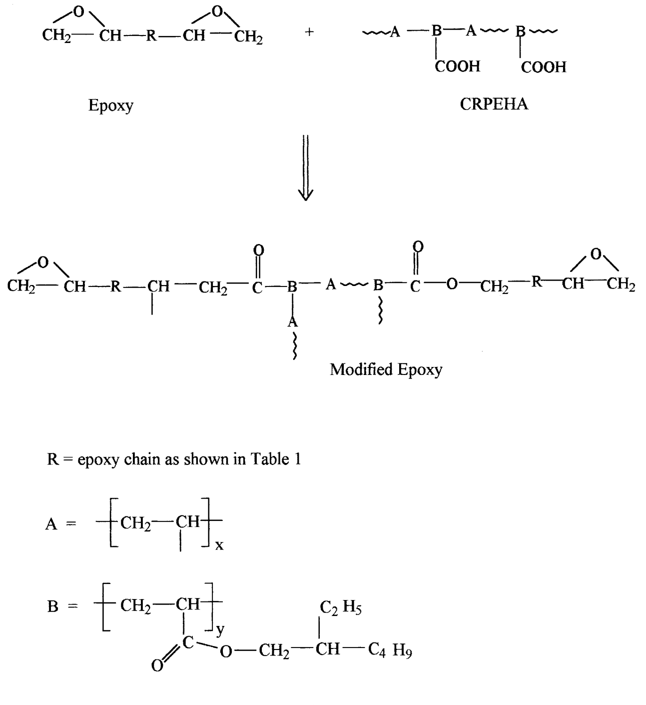


Fig. 1. Prereaction of epoxy with CRPEHA.

Table 3
Carboxyl group concentration and viscosity of liquid rubber modified epoxy before and after precuring

Sample	Carboxyl content (mequiv./g)		Viscosity (Pa s)	
	Before precure	After precure	Before precure	After precure
Epoxy/LR-1	0.05	0	6.7	10.2
Epoxy/LR-2	0.10	0	7.3	15.6
Epoxy/LR-3	0.14	0	7.8	16.1
Epoxy/LR-4	0.23	0	9.4	18.7

epoxy formulations [32,33]. It is clear from the figure that the extent of reduction in T_g gradually increases with increase in the functionality of the liquid rubber. This indicates that though all the liquid rubbers were added in the same concentration, the amount of liquid rubbers which remains dissolved in the epoxy matrix, is different for different liquid rubbers. The highest depression of T_g (30 K) in case of epoxy/LR-4 indicates the higher extent of the dissolved rubber. This can be explained by considering the solubility parameter concept.

The solubility parameter of epoxy is 21.05 $(\mathrm{J/cm^3})^{0.5}$. Thus, the proximity of the solubility parameter between the liquid rubber and the epoxy resin, becomes closure and closure from LR-1 to LR-4 leading to their better miscibility with epoxy resin. Moreover, with the increase in the functionality of liquid rubber the chemical interaction between the rubber and the epoxy matrix increases which induces compatibility of the rubber with epoxy. Similar observation was reported by Wang et al. [34] using epoxy functionalized poly(butyl acrylate) oligomer as a toughening agent.

3.4. Mechanical properties of the modified epoxy networks

The results for tensile testing of the unmodified epoxy and modified epoxy networks are presented in Table 5. The tensile strength of the modified epoxy networks are lower than that of the unmodified epoxy. This can be attributed to the presence of low modulus rubber into the epoxy matrix [32,33]. It is also observed that the tensile strength of the modified network decreases and the % elongation at the break increases with increase in the functionality of the liquid rubbers (LR-2 to LR-4) indicating flexibilizing effect. Flexibilizing effect as reflected also in the reduction of T_g can be attributed to the dissolution of certain amount of rubber. Maximum reduction in tensile strength occurs in case of LR-4.

Table 4
Gel time of the modified epoxy samples

Resin	Gel time at 27°C (min)
Epoxy	22
Epoxy/LR-1	32
Epoxy/LR-2	36
Epoxy/LR-3	35
Epoxy/LR-4	41

A similar trend was found in case of flexural properties (Table 5). Both the flexural strength and flexural modulus decrease and flexural strain increases with increasing functionality of the liquid rubber. In the cases of LR-2 ($f = 1.8$) and LR-3 ($f = 2.5$), there is only modest decrease in modulus as a result of modification compared to neat epoxy whereas drastic reduction in modulus occurs in case of LR-4. However, epoxy/LR-1 shows inferior tensile and flexural properties. The odd result in case of LR-1 will be explained shortly in terms of morphology analyzed SEM.

The results for impact strength of unmodified and modified epoxy networks are shown in Fig. 3. With the incorporation of LR-1 having only a few carboxyl groups ($f = 1.2$), toughening becomes less effective due to limited capacity for stress transfer between the epoxy matrix and the dispersed modifier phase. It is clear from the figure that impact energy increases when functionality of liquid rubber is increased from 1.2 to 1.8. This can be attributed to the increase in interfacial adhesion between the rubber and the epoxy [26,27,33]. When functionality is further increased to 2.5, there is no significant change in impact energy. This suggests that adhesion is important up to a critical value and fracture energy is not enhanced by the added adhesion. In case of LR-4 ($f = 4.4$), the impact strength is still high compared to the unmodified epoxy. However, the value of impact strength is significantly lower than that observed in

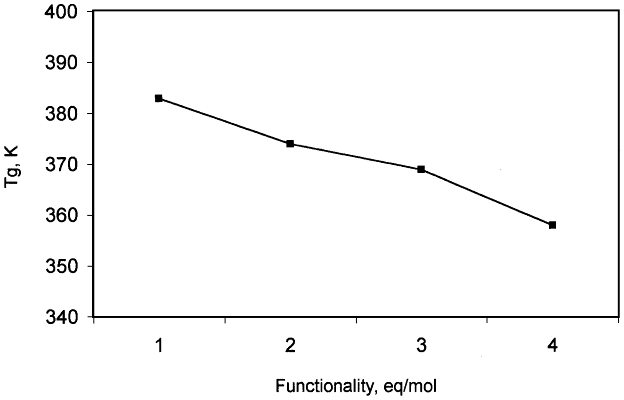


Fig. 2. Effect of carboxyl functionality of liquid rubber on the T_g of modified networks.

Table 5
Effect of CRPEHA modification on the mechanical properties of modified epoxy networks

Resin	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural strain (%)	Flexural modulus (MPa)
Epoxy	52.4	3.2	140	1.9	7325
Epoxy/LR-1	36.2	3.0	96	2.0	4728
Epoxy/LR-2	48.1	4.1	128	3.2	6265
Epoxy/LR-3	46.7	4.5	124	3.6	6123
Epoxy/LR-4	34.3	6.7	95	4.7	4570

the case of LR-2 ($f = 1.8$). This will be explained in terms of the morphology seen by SEM.

The value of impact strength of epoxy/LR-2 is 39.6 J/m, which is more than twice that of the neat epoxy (19.2 J/m). The improvement in impact strength is comparable to that reported for ambient temperature curable epoxy systems using CTBN and CTPEHA as the toughening agents [19,35]. However, unlike CTPEHA, which results in the improvement of impact energy without a significant change in T_g, in case of CRPEHA, the improvement in impact energy is accompanied with a modest sacrifice in glass transition temperature due to dissolution of some amount of rubber.

3.5. Morphology

The SEM photographs for the fracture surfaces of unmodified and modified epoxy networks are shown in Fig. 4. From the photograph (Fig. 4a), it can be seen that a smooth glassy fractured surface with cracks in different planes, for the case of unmodified epoxy. This indicates brittle fracture of the unmodified epoxy, which accounts for its poor impact strength.

The LR-1, LR-2, LR-3 modified epoxy networks show a two-phase morphology. On the other hand, LR-4 modified epoxy network shows a single-phase morphology. This can be attributed both to the effects of solubility parameter and chemical interaction.

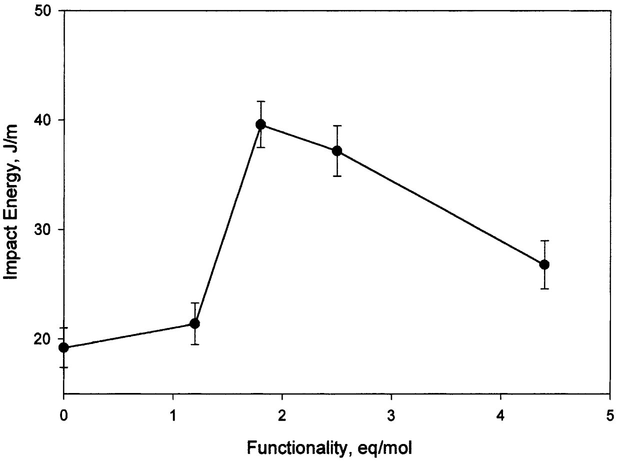


Fig. 3. Effect of carboxyl functionality of liquid rubber on the impact strength of modified networks.

Combining the Flory–Huggins equation and the Hildebrand equation [36], the free energy of mixing can be expressed as

$$\frac{\Delta G_m}{V} = \phi_e\phi_r(\delta_e - \delta_r)^2 + RT\left(\frac{\phi_e}{V_e}\ln\phi_e + \frac{\phi_r}{V_r}\ln\phi_r\right) \quad (2)$$

where ϕ_e, ϕ_r are the volume fractions, δ_e, δ_r the solubility parameters and V_e, V_r the molar volumes of epoxy and rubber, respectively. Since ϕ_e, ϕ_r are fractions (<1), the second term (change in entropy) is always negative. As the epoxy resin cures, the value of V_e and V_r increases which results in a decrease in second term. At a critical conversion ΔG_m becomes positive and phase separation occurs. However, if $(\delta_e - \delta_r)$, i.e. the difference between the solubility parameters of the epoxy and the liquid rubber is very low, then the change in entropy due to the curing reaction, cannot make free energy change of mixing (ΔG_m) positive prior to gelation. In the case of LR-4, $\delta_e \sim \delta_r$ is less than 0.2, which explains the homogeneity of this system. In addition, the liquid rubber has a higher functionality and undergoes extensive chemical reactions with the epoxy, which further makes phase separation more difficult. This observation that the liquid rubber having higher functionality does not phase separate from the matrix is consistent with the experimental findings of Bell at al. [37,38] and Lee et al. [39].

The micrograph for epoxy/LR-1 shows poor interfacial adhesion between epoxy and rubber phase and rubber phase is not uniformly dispersed. The poor adhesion can be attributed to the low functionality of LR-1 ($f = 1.2$, Table 1). This explains the inferior performance of epoxy/LR-1.

The micrograph for epoxy/LR-2 (Fig. 4c) shows uniform distribution of rubber microdomains and good adhesion of the rubber phase with the epoxy matrix. This can be attributed to higher functionality of LR-2 ($f = 1.8$, Table 2) through which it forms strong chemical bonds with the epoxy. It is also observed that microdomains are connected, unlike the discrete globular morphology reported by many authors [32,33,35] in various rubber toughened epoxy systems. Yamanaka et al. [40] reported interconnected microstructure in the case of RT curing CTBN modified epoxy system. They have attributed it to the phase separation by spinodal decomposition. They also reported that the interconnected morphology leads to higher toughness compared to globular morphology observed in case of high temperature curing epoxy system.

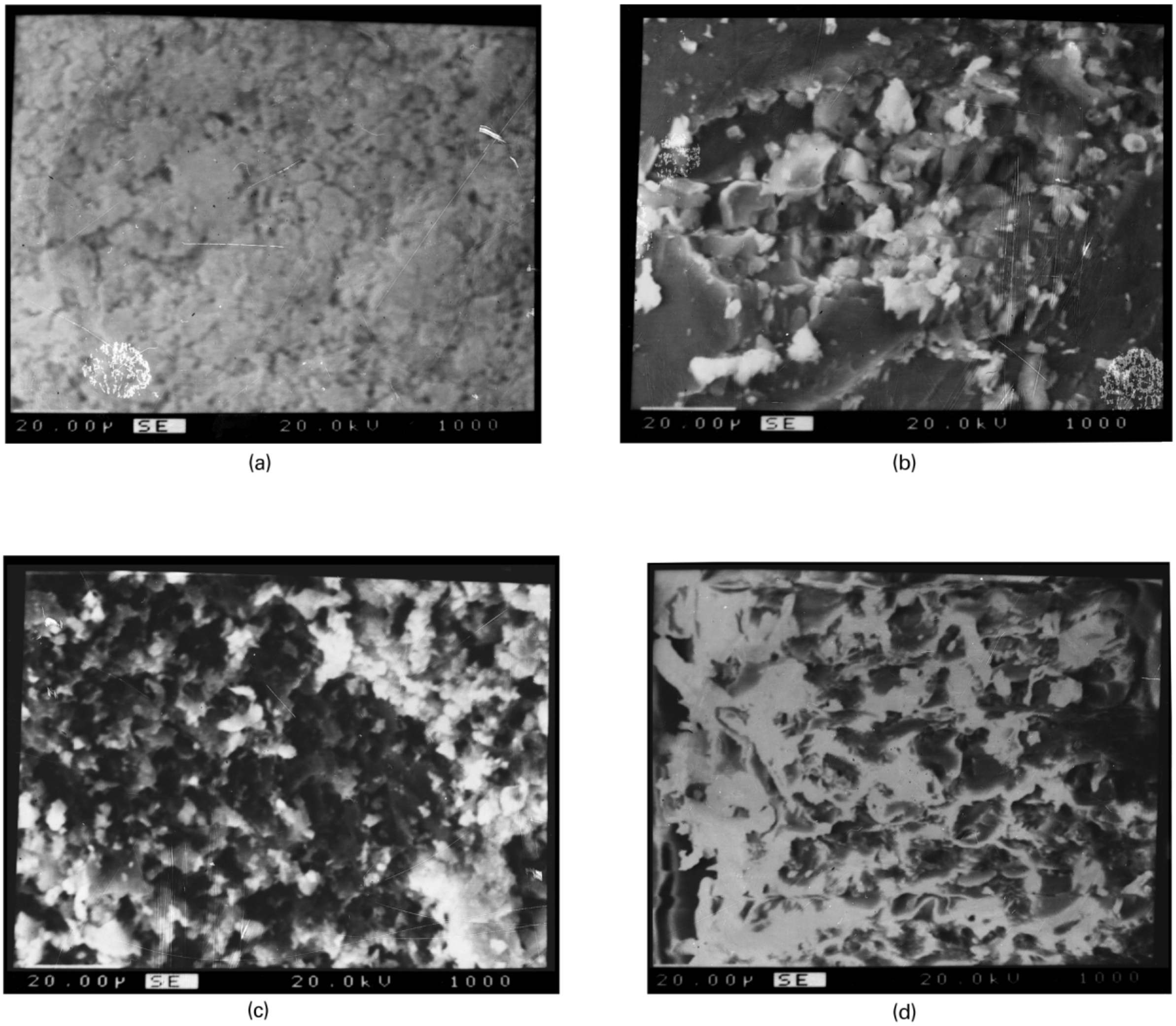


Fig. 4. SEM microphotographs of the fracture surfaces for (a) unmodified epoxy; (b) epoxy/LR-1; (c) epoxy/LR-2; (d) epoxy/LR-4.

Flexan et al. [41] reported discrete and continuous microstructure as a function of rubber concentration and argued that continuous microstructure leads to a higher toughness. Sue et al. [42] found a modest improvement in the fracture toughness of a DGEBA/diaminodiphenyl sulfone (DDS) system modified with core-shell rubber particles when particles have a connected morphology compared to a discrete microstructure. In a similar type of study using a DGEBA/piperidine system, Bagheri et al. [43] reported a significantly higher toughness in case of continuous morphology compared to discrete microstructure. The reason lies in the fact that connected morphology enables shear bands to grow further at the crack tip. Therefore, the enlargement of the crack tip plastic zone is the reason for the superiority of the connected microstructure. However, the optimum extent of connectivity is yet to be established.

The epoxy/LR-2 system contains some extent of dissolved rubber as evident from tensile test (Table 5) and the reduced value of T_g (Fig. 2). The increase in ductility of the matrix caused by the dissolved rubber enhances the effectiveness of the toughening process [44]. Hence both the toughening and flexibilizing effects can operate, resulting in the maximum improvement of impact strength.

The fracture surface of epoxy/LR-4 is very rough and indicates massive plastic deformation. Energy is absorbed during plastic deformation in case of the modified epoxy network giving rise to a higher toughness and impact strength [45]. However, the improvement in impact strength is less in a system where epoxy and rubber phase have been rendered miscible and no phase separated rubber exists. Thus, although epoxy/LR-4 system has high impact strength compared to unmodified epoxy, it is not as effective as for incorporation of LR-2.

3.6. 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 using HY 960 is more brittle and has

Table 6
Effect of matrix ductility on toughening of epoxy resin modified with LR-2

Material	Impact energy (J/m)
Unmodified epoxy[a]	19.2 ± 1.8
Modified epoxy[a]	39.6 ± 2.1
Unmodified epoxy[b]	10.3 ± 1.7
Modified epoxy[b]	16.5 ± 1.3

[a] Cured by HY 951.
[b] Cured by HY 960.

lower impact energy as compared to the network made by using HY 951. The lower fracture resistance of the LY 556/HY 960 system with respect to the LY 556/HY 951 system can be explained in the light of the chemical structures of the hardeners (Table 1). HY 960 contains rigid aromatic ring whereas HY 951 contains flexible aliphatic chain. The impact energies of LR-2 modified epoxy networks and unmodified networks are shown in Table 6. It is clear from the table that improvement of fracture energy is more in case of the network cured with HY 951, which is more ductile.

The importance of ductility of the matrix has been reported in the modification of epoxy resin with liquid rubber like CTBN [46–48]. CTBN acts as an effective toughening agent for piperidine cured epoxy resin, but is less effective in the case of an epoxy/DDS system [49]. Levita et al. [50] 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.

4. Conclusion

The CRPEHA liquid rubbers can ideally be synthesized by solution polymerization. The CRPEHA oligomers having carboxyl functionality close to 2 and able to toughen epoxy resin effectively with a modest sacrifice of T_g and modulus. The impact energy of the modified network increases when functionality of the liquid rubber is increased to 2, due to increase in interfacial adhesion. The impact energy is not enhanced by further increase in adhesion. The liquid rubbers having higher carboxyl functionality ($f > 2.5$) do not undergo phase separation and lead to single-phase morphology. It is clear that a phase-dispersed morphology is desirable to cause maximum toughness and also to maintain in the value of T_g and modulus. The toughenability of the epoxy matrix increases with an increase in ductility of the matrix.

Acknowledgements

Authors are thankful to DST, New Delhi, India, for awarding a BOYSCAST fellowship to one of us (D.R).

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