

# Synthesis, Characterization, and Evaluation of Carboxyl-Terminated Poly(ethylene glycol) Adipate-Modified Epoxy Networks: Effect of Molecular Weight

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Received 10 April 2006; accepted 22 May 2006

DOI 10.1002/app.25285

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of carboxyl-terminated poly(ethylene glycol) adipate (CTPEGA) was synthesized by polycondensation of poly(ethylene glycol) (PEG) of various molecular weights ("2000," "4000," "6000," "8000," "10,000" g/mol) and adipic acid. CTPEGA was incorporated into the epoxy by a prereaction method. The CTPEGA and modified epoxy samples were thoroughly characterized by Fourier transform infrared spectroscopy,  $^1\text{H}$  NMR spectroscopy, differential scanning calorimetry, and gel permeation chromatography. The effects of molecular weight of CTPEGA on thermomechanical and viscoelastic properties of the modified epoxy networks were investigated. Maximum improvement in impact strength

was found for the epoxy network modified with CTPEGA containing PEG of molecular weight 2000 g/mol. With further increase in molecular weight of CTPEGA, the impact strength of the modified network decreases. However, in case of higher molecular weight CTPEGA, the improvement in toughness was achieved without any reduction in  $T_g$  due to the complete phase separation. The results were explained in terms of morphology studied by scanning electron microscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1723–1730, 2007

**Key words:** epoxy; poly(ethylene glycol); toughening; impact

## INTRODUCTION

Epoxy resins are a class of versatile thermosetting polymers, which are widely used in structural adhesives, composites, and surface coatings.<sup>1</sup> The unique properties such as good adhesion strength, low cure shrinkage, low creep, excellent corrosion and weather resistance, elevated temperature workability, and insulation properties allow these materials to be a better candidate in the field of protective coatings, electronic (potting, packing of integrated circuits, and light emitting diode), and aircraft (fiber-reinforced plastic) industries.<sup>2–4</sup> The major drawback of epoxy resins is that in the cured state they are brittle materials having impact energy of about two orders of magnitude lower than that of engineering thermoplastics and three orders lower than that of metals.<sup>5</sup> This inherent brittleness causes poor damage tolerance to impact of the composites made from epoxy resin and poor peel and shear strength of epoxy-based adhesives.

Toughening of epoxy without compromising the thermal and mechanical properties is a subject of considerable research interest. Toughness implies energy absorption and is achieved through various deforma-

tion mechanisms before the failure occurs during the crack propagation. Enhancing the toughness by reducing crosslink density or using plasticizers results in increase of the plastic deformation. Besides, it also greatly affects the modulus and thermal properties of the epoxy networks. One effective method to increase the toughness is to blend with a reactive liquid rubberlike carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN),<sup>6–10</sup> which is initially miscible with the epoxy and undergoes phase separation on curing, leading to the formation of a two-phase microstructure. Such a two-phase system having a small amount of rubber (10–15 wt %) often shows outstanding impact strength as the rubber particles, dispersed and bonded to the epoxy matrix, act as centers for dissipation of mechanical energy by cavitation and shear yielding.<sup>11,12</sup> The improvement in fracture toughness is generally achieved without a significant reduction in thermal and mechanical properties of the crosslinked epoxy networks.

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.<sup>13</sup> The presence of double bonds in the chain can cause oxidation reaction and further crosslinking with the loss of elastomeric properties and ductility of the precipitated particles.<sup>14</sup> Secondly, there remains a possibility that traces of free acrylonitrile, which is carcinogenic,

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might exist and limit the use of these materials.<sup>15</sup> The saturated liquid rubbers such as siloxane,<sup>16</sup> polyurethane,<sup>17,18</sup> acrylates,<sup>19–22</sup> etc. have been reported as an alternative to CTBN. Various types of ductile thermoplastics were also studied as an alternative to reactive rubber for improving the toughness of the epoxy resinlike poly(ether imides),<sup>23</sup> poly(aryletherketone),<sup>24</sup> poly(phenylene oxide),<sup>25</sup> functionalized polyesters,<sup>26</sup> and polysulfones.<sup>27</sup> Recently, use of hyperbranched polymers,<sup>28–30</sup> layered silicates,<sup>31</sup> and liquid crystalline modifier<sup>32</sup> has been reported.

Poly(ethylene glycol) (PEG) is reported to increase toughness of epoxy as well as other polymers because of the presence of flexible ether linkages.<sup>33–39</sup> In all these studies, PEG has been used to blend physically with the base polymer to be modified. Ratna et al.<sup>40–42</sup> reported carboxyl-terminated PEG adipate (CTPEGA) as a modifier for epoxy, describing about chemical bonding of epoxy matrix via carboxyl functional groups. CTPEGA was successfully utilized to modify epoxy resin, which also offers better processibility compared to the conventional liquid rubbers.<sup>43</sup> By using PEG up to molecular weight of 1000 g/mol, they found that CTPEGA forms compatible blend with epoxy and resulted in significant improvement in toughness. The advantage of PEG-based modifier compared to the conventional toughening agents is that they are absolutely nontoxic in nature. The toxicity aspects are very important when a material has to be applied in the interior, especially in a closed compartment as in the naval applications. However, in case of low molecular weight CTPEGA, the improvement in toughness was achieved with a significant sacrifice in  $T_g$ . The objective of the present work is to study the effect of molecular weight of PEG on the thermomechanical behavior and morphology of the modified epoxy networks to achieve high toughness without compromising the thermal properties. The detailed synthesis and characterization of CTPEGA of various molecular weights, thermomechanical properties, and morphology of the blends will be discussed in this article.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) (PEG) having weight-average molecular weight "2000," "4000," "6000," "8000," "10,000" g/mol (Fluka, Switzerland), adipic acid (AA) (S.D. Fine Chem., India), para toluene sulfonic acid (PTSA) (LOBA Chemicals, India), triphenyl phosphine (TPP) (SISCO, India), and petroleum ether (boiling point 40–60°C) (S.D. Fine Chem., India) were used as received. Epoxy resin was a liquid diglycidyl ether of bisphenol-A type (DGEBA) (Vantico, Araldite LY556) with an equivalent weight per epoxide group of

195 ± 5. An ambient temperature hardener, triethylene tetramine (TETA, Vantico, HY951) (amine equivalent 26 ± 2), was used as a curing agent. All other reagents were of analytical grade and used as received.

### Characterization methods

Carboxyl content of carboxyl-terminated PEG adipate (CTPEGA) was determined by titration with methanolic solution of 0.1N KOH, using chloroform/isopropyl alcohol mixture ratio 2 : 1 (v/v) as a solvent and phenolphthalein as an indicator.

Infrared spectra were taken in a Fourier transform infrared (FTIR) spectrophotometer (Perkin-Elmer, model 1650). CTPEGA and modified resin solution in chloroform were spread on a sodium chloride window and the spectrum of dry film was recorded.

<sup>1</sup>H spectra were recorded on a 500-MHz FTNMR instrument (Bruker Avance-500) with CDCl<sub>3</sub> as a solvent and tetramethylsilane as an internal standard and the values are reported in δ unit.

Molecular weight distribution of polymers were determined by gel permeation chromatography (GPC Waters 2610) separation module having 2410 refractive index detector, HR 1 and HR 4 columns, calibrated with linear polystyrene standards, tetrahydrofuran (THF) was used as a solvent. About 0.25% of the liquid resin was dissolved in THF and filtered before use. The flow rate was maintained at 0.7 mL/min.

Differential scanning calorimetry (DSC) instrument (Dupont 910) was used for determining thermal transitions of CTPEGA. A heating rate of 10°C/min, sample weight of about 20 mg, and a nitrogen flow rate of 60 mL/min were maintained during all the experiments.

Epoxy content of the resin was determined by standard titration method, using hydrogen bromide in acetic acid as described in the literature.<sup>44</sup>

Dynamic mechanical thermal analyzer (DMTA MK III, Rheometric Scientific) was employed for measuring dynamic mechanical properties of cured modified epoxy networks at a fixed frequency of 1 Hz, with a heating rate of 3°C/min. A dual cantilever mode was used for samples of size 20 × 10 × 2 mm<sup>3</sup>.

Viscosity measurement on the uncured modified liquid resin was carried out by Haake Rotoviscometer (Haake RVIII) at shear rate range of 0–100 s<sup>-1</sup> at 27°C, using MV III head having clearance of 0.96 mm between the concentric cylinders of the viscometer.

Izod notched impact test for cured, notched CTPEGA-modified (CR1 to CR-5), and pure epoxy was carried out using a Tinius Olsen impact tester (Willow grove, PA) with a striking velocity of 3.46 m/s. The impact specimens were cast in a teflon mold with built-in arrangement for notch, according to ASTM D-256. The impact test was carried out at room temperature and the impact energy was reported in Joule per

meter. Average of the results of 10 notched samples are reported.

A low voltage scanning electron microscope (SEM) JEOL-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" examinations. Photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

The measure of percentage of water uptake by pure and modified epoxy networks was carried out in seawater at room temperature, according to ASTM D471-79, at an interval of 5 days up to 1 month.

### Synthesis and characterization of CTPEGA

On the basis of different molecular weights of PEG, CTPEGA samples were synthesized by the reaction of corresponding PEG with adipic acid, as in the method described by Deb et al.<sup>40</sup> In a typical recipe solid, PEG 2000 (200 g; 0.1 mol), adipic acid (21.9 g; 0.15 mol), PTSA (1.11 g; 0.5%), and toluene (67 mL; 30%) were poured in a three necked reaction flask fitted with a mechanical stirrer, a nitrogen inlet, and a Dean and Stark condenser. The temperature of the reaction was maintained at 165°C in silicone oil bath and the water formed during the reaction was removed continuously from the reaction mixture via azeotrope formation with toluene. The reaction was monitored from the amount of water collected.

After "completion" of reaction (the reaction time was about 4 h), the reaction mixture was subjected to distillation under reduced pressure at 70°C for removing solvent, and the residual liquid was poured "into an excess" amount of petroleum ether (boiling point 40–60°C) for purification. The collected solid was filtered, dried, and stored in an airtight container. The final solid product was then characterized. The reaction scheme is same as described earlier.<sup>40</sup>

FTIR (KBr) ( $\text{cm}^{-1}$ ): 2871 (C—H aliphatic), 3512 (acid —OH), 1642 (acid —C=O);  $^1\text{H}$  NMR ( $\delta$  ppm; solvent- $\text{CDCl}_3$ ): 8.0 (s, —OH of acid), 7.2 (m,  $\text{CDCl}_3$ ), 1.3–1.4 (m, — $(\text{CH}_2)_n$ —), 2.8–4.4 (m, — $(\text{CH}_2\text{—CH}_2\text{—O})_n$ —).

### Synthesis and characterization of modified epoxy (MR-1–MR-5)

The dried solid CTPEGA samples of different molecular weights were reacted with epoxy resin, using TPP as a catalyst. In a typical formulation, epoxy resin (100 g) LY 556 (DGEBA), CTPEGA (20 g), and triphenyl phosphine (1 g) were mixed and heated at 100°C under nitrogen atmosphere until all carboxyl groups were completely reacted.

FTIR (NaCl window) ( $\text{cm}^{-1}$ ): 1734 (ester), 2923 (C—H, aliphatic), 3052 (C—H, aromatic), 1607, 1508 (aromatic C=C), 914, 833 (epoxy ring);  $^1\text{HNMR}$  ( $\delta$  ppm; solvent- $\text{CDCl}_3$ ): 2.7–3.3 (m, epoxy ring), 6.7–7.0 (m, aromatic), 7.2 (m,  $\text{CDCl}_3$ ).

### Curing of modified epoxy

All the modified resins (MR-1 to MR-5) were analyzed for their epoxy equivalent and accordingly required amount (26 g for one equivalent of epoxy) of TETA was added and thoroughly mixed. The mixture was then degassed and cast in a teflon mold of size 150 mm  $\times$  150 mm  $\times$  2.5 mm and cured at room temperature for 24 h. The samples were postcured at 120°C for 2 h.

## RESULTS AND DISCUSSION

### Synthesis and characterization of CTPEGA

CTPEGA of different molecular weights were made by varying the molecular weights of PEG used in the polycondensation reaction. The molecular weights and molecular weight distribution of the CTPEGA samples were determined by GPC, using linear polystyrene standards with a refractive index detector. It may be noted that because of the use of an equivalent polystyrene standard and a refractive index detector instead of a mass detector, the molecular weight values are very approximate. For comparison purpose, the molecular weight data are designated as apparent molecular weight. The apparent number-average and weight-average molecular weight and polydispersity index (PDI) values of the polymers are shown in Table I. From the table, it was observed that molecular weight of CTPEGA increased with increase in the molecular weight of PEG. All the polymers are having PDI in the range of 1.3–1.5. The number-average molecular weights measured by an end group analysis are higher than those measured by GPC. In addition to above two reasons, this can be attributed to the presence of carboxyl groups, which cause specific intermolecular interactions inside the GPC column.<sup>21</sup> This interaction prolongs the retention time, which is inversely related to  $M_n$ .

The structure of CTPEGA was confirmed by FTIR and  $^1\text{H}$  NMR spectroscopy.<sup>45</sup> DSC scans of the CTPEGA were shown in Figure 1. From the figure, it is clear that the melting point of CTPEGA is lower than that of the pure PEG.<sup>35,36</sup> This may be due to a decrease in crystallinity of PEG as a result of the incorporation of flexible alkyl units from the adipic acid.

### Modification of epoxy with CTPEGA

For an effective toughening, the modifier is required to be chemically bonded to the epoxy matrix.<sup>40,43,46</sup>

TABLE I  
Physicochemical Properties of CTPEGA<sup>a</sup> and Modified Epoxy Resins<sup>b</sup>

Samples	Molecular weight <sup>c</sup>			Viscosity (m·Pa·s) <sup>d</sup>	Epoxy equivalent <sup>e</sup>
	$M_n$	$M_w$	PDI		
CTPEGA-1	2312 (2362)	3788	1.81	–	–
CTPEGA-2	3005 (3985)	4300	1.43	–	–
CTPEGA-3	4841 (6734)	6974	1.44	–	–
CTPEGA-4	5880 (7146)	9289	1.57	–	–
CTPEGA-5	6775 (7342)	11044	1.63	–	–
MR-1	3999	5147	1.28	10200	235
MR-2	4349	5830	1.34	11000	230
MR-3	6269	9763	1.55	11200	231
MR-4	8194	12723	1.55	14500	232
MR-5	8537	13167	1.54	14100	223
LY556	–	–	–	8750	186

<sup>a</sup> Values in parentheses are the values determined by titration with methanolic solution of 0.1N KOH using chloroform/isopropyl alcohol mixture and phenolphthalein as an indicator.

<sup>b</sup> Modified epoxy resin prepared from corresponding CTPEGA 1 to CTPEGA 5.

<sup>c</sup> Determined by gel permeation chromatography.

<sup>d</sup> Measured in Haake Rotoviscometer (Haake RVIII) at shear rate range of 0–100 s<sup>-1</sup> at 27°C.

<sup>e</sup> Determined by standard titration method, using hydrogen bromide in acetic acid.

For that reason, the synthesized solid CTPEGA was reacted with the epoxy by using TPP as a catalyst in an inert atmosphere. The reaction is a carboxyl–epoxy esterification reaction as proposed by Romanchick et al.<sup>47</sup> The product was an epoxy end-capped PEG adipate, which can be cured with the same hardener. The reaction scheme is illustrated in Figure 2. Since equivalent weight of CTPEGA (4000) is 20 times higher than the equivalent weight of epoxy, the epoxy remains in the mixture in a large molar excess, which essentially prevents the further polymerization.

The physicochemical properties of modified epoxy resins (MR-1 to MR-5) shown in Table I. From the table, it is clear that the viscosity of the modified epoxy resin increases with increase in molecular weight

of CTPEGA due to the increase in chain length of the polymer as expected. The epoxy equivalent of modified epoxy are higher than the pure epoxy, due to participation of epoxy group during prereaction with CTPEGA.

### Viscoelastic properties of CTPEGA-modified epoxy networks

To study the effect of CTPEGA modification on viscoelastic properties, the pure epoxy and the modified epoxy networks were studied by DMTA analysis. Tan  $\delta$  versus temperature plots for pure epoxy and modified epoxy networks, based on CTPEGA having various molecular weights, are shown in Figure 3. It is

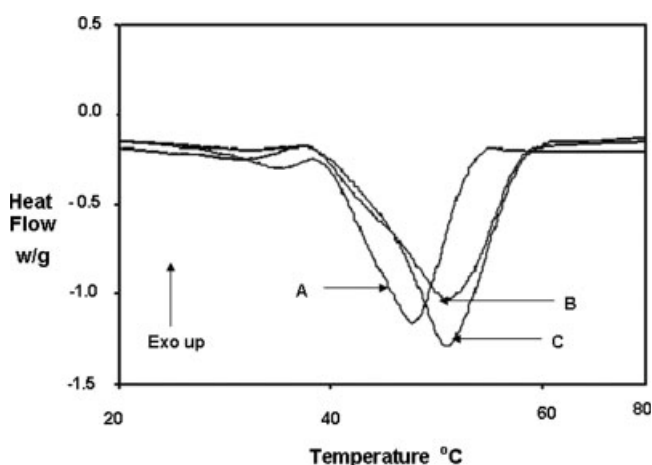


Figure 1 DSC scans of CTPEGA; (A) CTPEGA-1, (B) CTPEGA-3, and (C) CTPEGA-5.

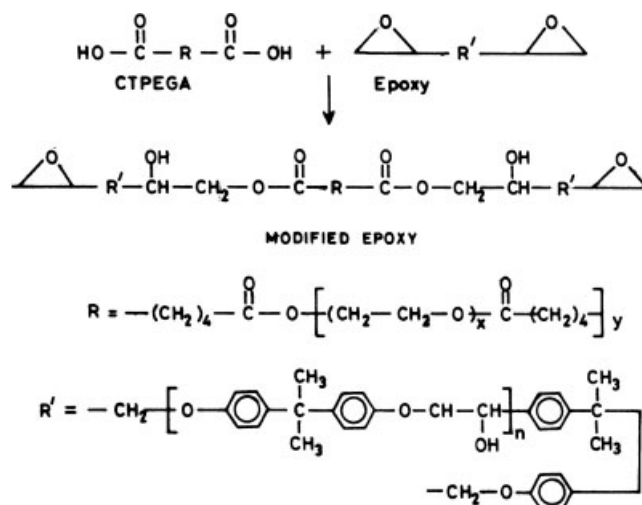
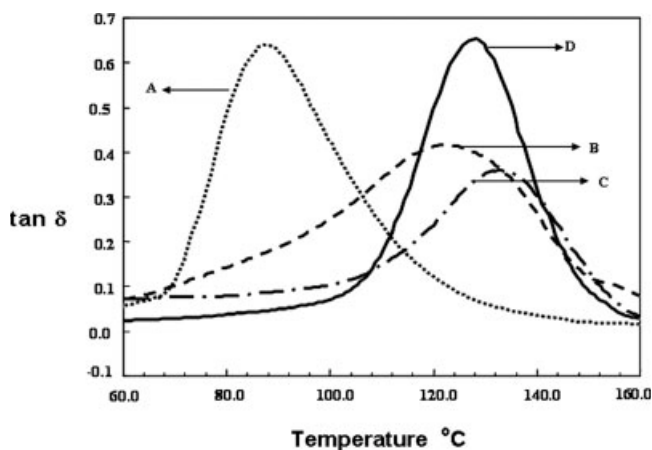


Figure 2 Modification of epoxy with CTPEGA.



**Figure 3** Tan  $\delta$  versus temperature plot of (A) CR-1, (B) CR-3, (C) CR-5, and (D) LY556.

observed that tan  $\delta$  peak temperature increases with increase in CTPEGA molecular weight. Moreover, beyond 8000 g/mol, the CTPEGA-modified epoxy shows tan  $\delta$  peak temperature at the same temperature as unmodified epoxy. This indicates that CTPEGA based on PEG of molecular weight of 8000 g/mol and above form immiscible blend with epoxy. However, the lower molecular weight CTPEGA is miscible completely or partially (semi compatible) with epoxy, resulting in decrease of tan  $\delta$  peak temperature.

The values of the storage modulus ( $E'$ ) at 35°C, tan  $\delta$  peak temperature ( $\alpha$  relaxation temperature) are given in the Table II. Low temperature transitions of pure epoxy and the modified networks are shown in Figure 4. The unmodified epoxy shows a broad peak at lower temperature (ca.  $-60^\circ\text{C}$ ). This broad peak can be identified as the  $\beta$  relaxation of the epoxy resin, which is often attributed to the glyceryl-like groups in DGEBA.<sup>30</sup> The modified epoxy shows peak at  $-40^\circ\text{C}$ , which can be attributed to the CTPEGA-

rich phase. The height of the loss peak increases with increase in molecular weight of the CTPEGA. In our previous studies,<sup>40–43</sup> we have shown that the loss peak increases with increase in concentration of phase-separated rubber. This indicates that though the same amount of CTPEGA is added to all the blends, the extent of dispersed phase increases with increase in molecular weight of CTPEGA, as increase in molecular weight decreases the combinatorial entropy of mixing.<sup>46</sup> The same observation has been confirmed by SEM studies.

Crosslink density values were calculated as per reported procedure<sup>48</sup> and the results are presented in Table II. It was observed that the crosslink density of all the modified epoxy networks were lower than that of the pure epoxy networks. This is obviously due to the chain extension of epoxy resin by the CTPEGA. It was also observed that the crosslink density increased with an increase in molecular weight of CTPEGA. This is because in case of higher molecular weight, total carboxyl functionalities will be less as the amount of modifier remains same in all the cases. So extent of modification will be more in case of CTPEGA of lower molecular weight.

### Scanning electron microscope studies

The effect of molecular weight of PEG on morphological parameters of the CTPEGA-modified networks were analyzed by SEM. The SEM photographs for the fracture surfaces of the unmodified epoxy and modified cured epoxy networks (“CR-1” to “CR-5”; cured modified network of corresponding modified resin “MR-1” to “MR-5”) are shown in Figures 5(a)–(d). It is clear from the photographs that the pure epoxy shows a single-phase morphology with cracks in different directions, which indicates the brittle failure. The modified epoxy networks consist of two distinct phases; CTPEGA-rich phase dispersed in the continu-

**TABLE II**  
Dynamic Mechanical, Impact, and Swelling Properties of Cured Pure and Modified Epoxy Networks

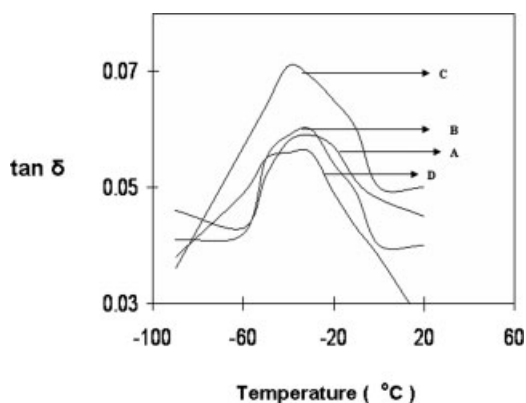
Resin	Storage modulus (GPa) <sup>a</sup>	$T_g$ ( $^\circ\text{C}$ ) <sup>a</sup>	Crosslink density ( $\text{mol}/\text{m}^3$ )	Impact strength ( $\text{J}/\text{m}^2$ ) <sup>b</sup>	Percentage of swelling <sup>c</sup>
CR <sup>d</sup> -1	0.76	87	4031	44.6	17.17
CR-2	0.93	113	4752	31.9	12.6
CR-3	0.90	122	5339	21.4	8.3
CR-4	0.95	127	5925	20.7	5.4
CR-5	1.03	132	7273	19.5	3.9
LY556	1.22	128	9864	12.8	1.7

<sup>a</sup> Measured from dynamic mechanical thermal analyzer networks at a fixed frequency of 1 Hz with a heating rate of  $3^\circ\text{C}/\text{min}$ .

<sup>b</sup> Measured from Tinius Olsen impact tester at room temperature.

<sup>c</sup> Carried out in seawater at room temperature, according to ASTM D471-79.

<sup>d</sup> Cured resins from corresponding modified resins MR-1 to MR-5.



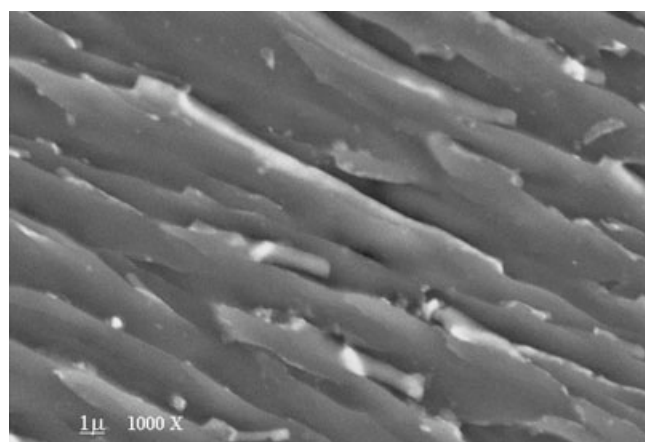
**Figure 4** Low temperature transition of CTPEGA-modified epoxy networks: (A) CR-1, (B) CR-3, (C) CR-5, and (D) LY556.

ous epoxy matrix except in case of CR-1 (CTPEGA based on PEG 2000) where the phase separation is not very clear. This is because CR-1 is a semicompatible

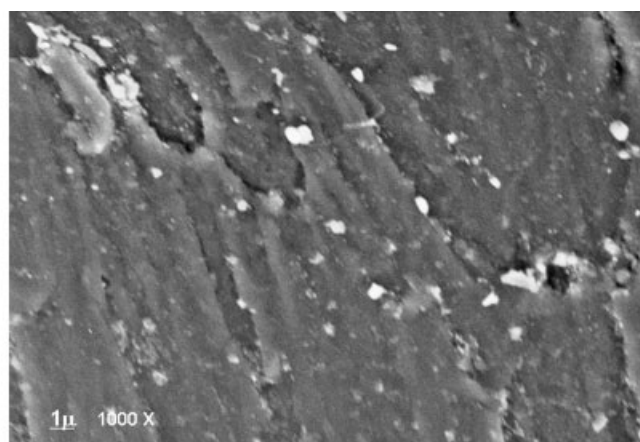
blend as evident from change in  $T_g$  analyzed by DMA.

It was also observed that microdomains are connected especially in case of higher molecular weight of CTPEGA, unlike the discrete globular morphology reported by many authors<sup>17,40-43,49,50</sup> in various rubber-toughened epoxy systems. Yamanaka et al.<sup>51</sup> reported interconnected microstructure in the case of room temperature curing CTBN-modified epoxy systems. 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 systems.

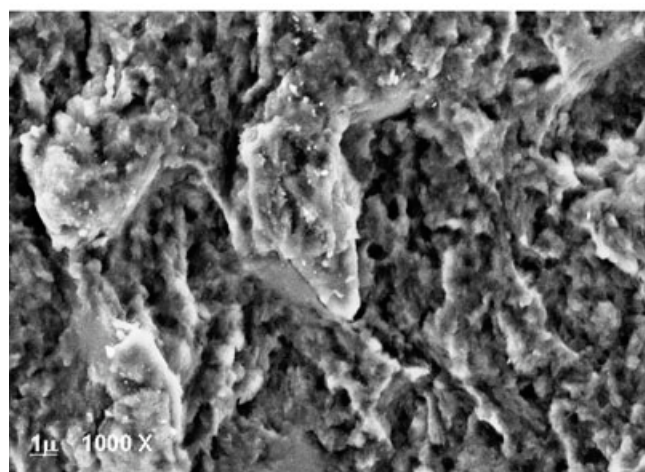
Flexman et al.<sup>52</sup> reported discrete and continuous microstructure as a function of rubber concentration and argued that continuous microstructure leads to a higher toughness. Sue et al.<sup>53</sup> found a modest improvement in the fracture toughness of a DGEBA/diaminodiphenylsulfone (DDS) system modified with



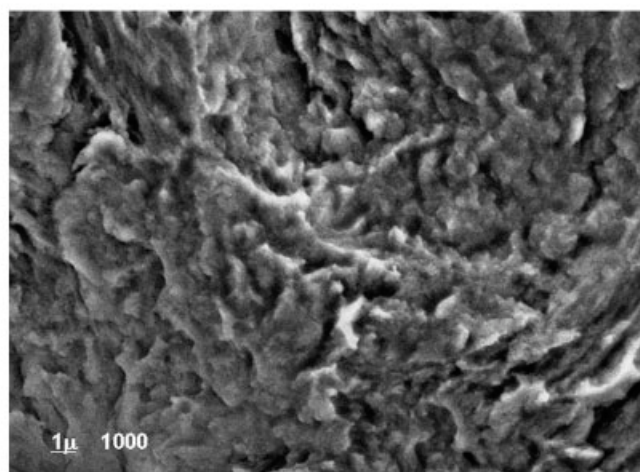
(a)



(b)



(c)



(d)

**Figure 5** SEM Photographs for the fracture surfaces of pure epoxy (DGEBA) and CTPEGA-modified epoxy networks: (a) LY556, (b) CR-1, (c) CR-3, and (d) CR-5.

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 and Pearson<sup>54</sup> reported a significantly higher toughness in case of a continuous morphology compared to a discrete microstructure. The reason lies in the fact that a 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.

### Impact properties

Impact energy data of cured pure epoxy and CTPEGA-modified epoxy networks (CR-1 to CR-5 and LY556) are presented in Table II. It was observed that all the modified networks showed higher impact strength compared to the unmodified epoxy. This improvement is higher compared to that achieved using low molecular weight CTPEGA as reported earlier.<sup>43</sup> It was also observed that the toughening effect decreased with increase in molecular weight of CTPEGA. This can be explained by considering two types of toughening mechanisms; one is the internal plasticization of epoxy matrix due to phase-mixing, which initiates massive shear deformation and another is second phase toughening. Second phase toughening involves dispersed rubber particles, which under triaxial stress cavitate and subsequently "release" the stress uniaxially and thereby initiate localized shear yielding in the matrix. The stress is transferred from one rubber particle to other through the matrix ligament and the shear yielding occurs throughout the deformation zone making the blend tough. In case of the lower molecular weight CTPEGA, there is no phase separation and hence the increase in impact strength is only due to the plasticizing effect. The epoxy/CTPEGA (2000) blend is semicompatible as discussed in DMA results and becomes incompatible with increase in molecular weight. Hence, in case of CTPEGA (2000), both the toughening mechanisms discussed above do operate, resulting in a large improvement in toughness. "It is to be noted" that both the mechanisms work in synergy as the performance of the dispersed particles increases with an increase in flexibility of the matrix due to enlargement of the deformation zones.<sup>47,55,56</sup> In case of higher molecular weight, only second phase toughening mechanism operates. Also the size of microdomain of the dispersed phase increases with increase in molecular weight of CTPEGA. It is well known that smaller microdomains are more effective for rubber cavitations and subsequent shear yielding, which is the major energy-dissipating mechanism in toughened epoxy networks.<sup>25,54</sup> That is why the

impact strength decreases with increase in molecular weight of CTPEGA.

### Percentage of water uptake of cured modified epoxy networks

Having achieved the desired mechanical properties, it is necessary to assess the water absorption properties of the modified networks with respect to the unmodified epoxy. This is particularly important when the adhesives made out of the modified epoxy have to work in marine environment or hot/wet conditions. In view of this, the cured modified epoxy (CR-1 to CR-5) and the pure epoxy samples were subjected to swelling study in seawater for a period of 1 month. Table II shows the % of water-uptake values of the cured resins. The water-uptake is found to be higher in all the modified epoxy networks compared to the pure epoxy network. It was also observed that the value decreased with the increase in molecular weight of CTPEGA. This can be explained in terms of crosslink density of the modified epoxy networks, which increases with increase in molecular weight of CTPEGA. The higher crosslink density makes the network more tight, resulting in reduced water diffusion (less water-uptake).

### CONCLUSIONS

Effect of CTPEGA molecular weight on thermomechanical and viscoelastic properties of the modified epoxy network was investigated. CTPEGA-2000 forms a semicompatible blend with epoxy and offers maximum improvement in toughness with significant reduction in  $T_g$ . With further increase in molecular weight of CTPEGA, the improvement in toughness decreases. However, with CTPEGA having molecular weight beyond 8000 g/mol, the improvement in toughness was achieved without any sacrifice in  $T_g$ . CTPEGA is a saturated modifier (no double bond) and absolutely nontoxic in nature. Hence, CTPEGA is a versatile modifier and the molecular weight of CTPEGA can be selected depending on the applications.

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