

# High Performance HTLNR/Epoxy Blend—Phase Morphology and Thermo-Mechanical Properties

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**ABSTRACT:** An attempt was made to toughen diglycidyl ether of bisphenol A (DGEBA) type epoxy resin with liquid natural rubber possessing hydroxyl functionality (HTLNR). Epon 250 epoxy monomer is cured using nadic methyl anhydride as hardener in presence of *N, N* dimethyl benzyl amine as accelerator. HTLNR of different concentrations up to 20 wt % is used as modifier for epoxy resin. The addition HTLNR to an anhydride hardener/epoxy monomer mixture has given rise to the formation of phase-separated structure, consisting of small spherical liquid natural rubber particles bonded to the surrounding epoxy matrix. The particle size increased with increase in rubber content. The viscoelastic properties of the blends were analyzed using dynamic mechanical thermal

analysis. The  $T_g$  corresponding to epoxy rich phase was evident from the dynamic mechanical spectrum, while the  $T_g$  of the rubber phase was overlapped by the  $\beta$  relaxation of epoxy phase. Glass transition of the epoxy phase decreased linearly as a function of the amount of rubber. The mechanical properties such as impact and fracture toughness were also carefully examined. The impact and fracture toughness increase with HTLNR content. A three-fold increase in impact strength was observed with 15 wt % HTLNR/epoxy blend. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 804–811, 2012

**Key words:** epoxy resin; liquid natural rubber; phase separation; subparticle formation; toughening

## INTRODUCTION

Epoxy resins are widely used in many industrial applications that range from common adhesives to sealant to matrix in high-performance materials.<sup>1,2</sup> The outstanding versatility of this resin is due to the great reactivity of the epoxy group that can react with different compounds like aliphatic and aromatic amines, anhydrides, polyamides, etc.<sup>3</sup> They are amorphous highly crosslinked polymers with excellent mechanical and thermal properties, high chemical and corrosion resistance, low shrinkage on cure etc. However, cured epoxy system is highly brittle. The inherent brittleness causes poor damage

tolerance and hence modification of epoxy resins to impart fracture toughness has been subject of intense research interest.<sup>4–10</sup> A few reports from the literature on rubber toughening and its relation with fracture morphology are summarized in the coming text. Bascom et al.<sup>11</sup> one among the first to study extensively on epoxy toughness, he observed that the size of plastic zones in rubber modified epoxies are related to the toughness. Later Yee and Pearson<sup>12–14</sup> presented TEM and SEM micrographs to support the notion that cavitation and plastic shear yielding of epoxy matrix are the micro deformation mechanisms occurring at the crack tip that dissipate energy and produce toughening effect. In an another study Riew et al.<sup>15,16</sup> demonstrated that the addition of Bisphenol A to the DGEBA/CTBN resin formulation increased the toughening effect of the rubber and he observed a bimodal distribution of particle size with a wide distribution of CTBN molecular weight during the early stage of curing. Recently, a new liquid rubber, reactive core/shell type hyperbranched block copolyether, was used for epoxy toughening by Fröhlich et al.<sup>17</sup> Even though there

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are various toughening mechanisms proposed by different researchers, it seems that a single theory is not sufficient to explain every experimental result and phenomenon of toughness.<sup>18–20</sup>

Despite the extensive work that has been dedicated to this topic, the literature review on epoxy/rubber suggest that continuous research is needed to develop advanced blends for future. Recently Ravindran et al.<sup>21</sup> reported a method for large-scale preparation of HTLNR by photochemical degradation in presence of H<sub>2</sub>O<sub>2</sub> and this method were followed in the present study. Though photo-depolymerization of natural rubber is a time consuming process, different molecular weights of liquid natural rubber can be obtained by varying the experimental conditions. The easy availability of the natural rubber in Kerala, India and its comparatively low cost favor the preparation of the epoxy–liquid natural rubber blends. In this work, we are using HTLNR prepared in our lab, for blending with epoxy, for better toughness. The main objective of this article is to analyse the dynamic mechanical properties and toughness of hydroxyl terminated liquid natural rubber (HTLNR) modified epoxy-anhydride system.

## EXPERIMENTAL

### Materials

Natural crumb rubber, Indian Standard Natural Rubber (ISNR 5L), having number average molecular weight ( $M_n$ -820,000), and intrinsic viscosity in Benzene at 30°C is 445 dL/g, was supplied by Rubber Research Institute of India, Kottayam. The characterization of ISNR-5L is given in Table I. Epoxy resin (LAPOX B-11), is a medium viscosity resin used mainly for solvent free coatings and building applications. LAPOX B-11 has epoxide index 5.2–5.5 eq/kg and epoxide equivalent 182–192 g/Eq, and viscosity 9000–12,000 MPa s at 25°C. Atul Polymers India Limited supplied curing agent, nadic methyl anhydride (K 68) and catalyst, benzyl dimethyl amine (BDMA). H<sub>2</sub>O<sub>2</sub> (30 wt %) supplied by E. Merck (India) was used for the photodegradation of natural rubber. E. Merck (India) also supplied toluene. All the chemicals were used as received without further purification. Throughout the study, the weight ratio of epoxy to anhydride was constant and equal to 100/80.

### Preparation of HTLNR

The photo depolymerization was carried out in a 5 wt % solution of NR (ISNR 5L) in toluene mixed with 30 wt % H<sub>2</sub>O<sub>2</sub> and methanol in volume ratio 20 : 1 : 3 respectively in a flat bottomed 1 L flask. Irradiation was carried out in sunlight with stirring for a period of 50 hours. The supernatant liquid was

TABLE I  
Characterization of ISNR-5L

Specification	ISNR-R	Sample used
1. Dirt content %Max.	0.10	0.08
2. Volatile matter (%)	0.8	0.6
3. Ash content (%)	0.75	0.62
4. Wallace plasticity $P_0$ , min.	30	43
5. PRI min.	60	68
6. Mooney viscosity $ML_{1+4}$ at 120°C	–	65–70

distilled to remove toluene and the liquid rubber (still contain little toluene) was separated. The sample for analysis was isolated from remaining toluene by precipitation with methanol. It was purified by reprecipitation from toluene solution two to three times using methanol. The product obtained was degassed and dried in a vacuum oven and were used for further analysis. HTLNR of any molecular weight can be prepared by the suitable choice of the exposure time. The molecular weight of the prepared HTLNR (used for our study) was determined to be  $M_n = 8400$  g/mol, and  $M_w = 46,000$ , PDI = 5.5 (GPC, PS standard) and the hydroxyl value was determined to be 17.44 (mg of KOH/g of rubber).

### Preparation of blends

Blends of epoxy resin/HTLNR containing 5, 10, 15, and 20 wt % HTLNR were prepared using the melt mixing technique. Epoxy resin and HTLNR were mixed under constant stirring at 120°C until a homogeneous solution was obtained. After proper mixing stoichiometric amounts of the curing agent, the anhydride, and the accelerator, a tertiary amine, was added to epoxy resin/HTLNR solution, and mix well for three to five minutes. The solution was then transferred into an open mould, kept at 120°C in a vacuum oven. It was then precured under ambient conditions for 30 min at 120°C, for 2 hour at 140, 150 and 180°C and then post cured at 200°C.

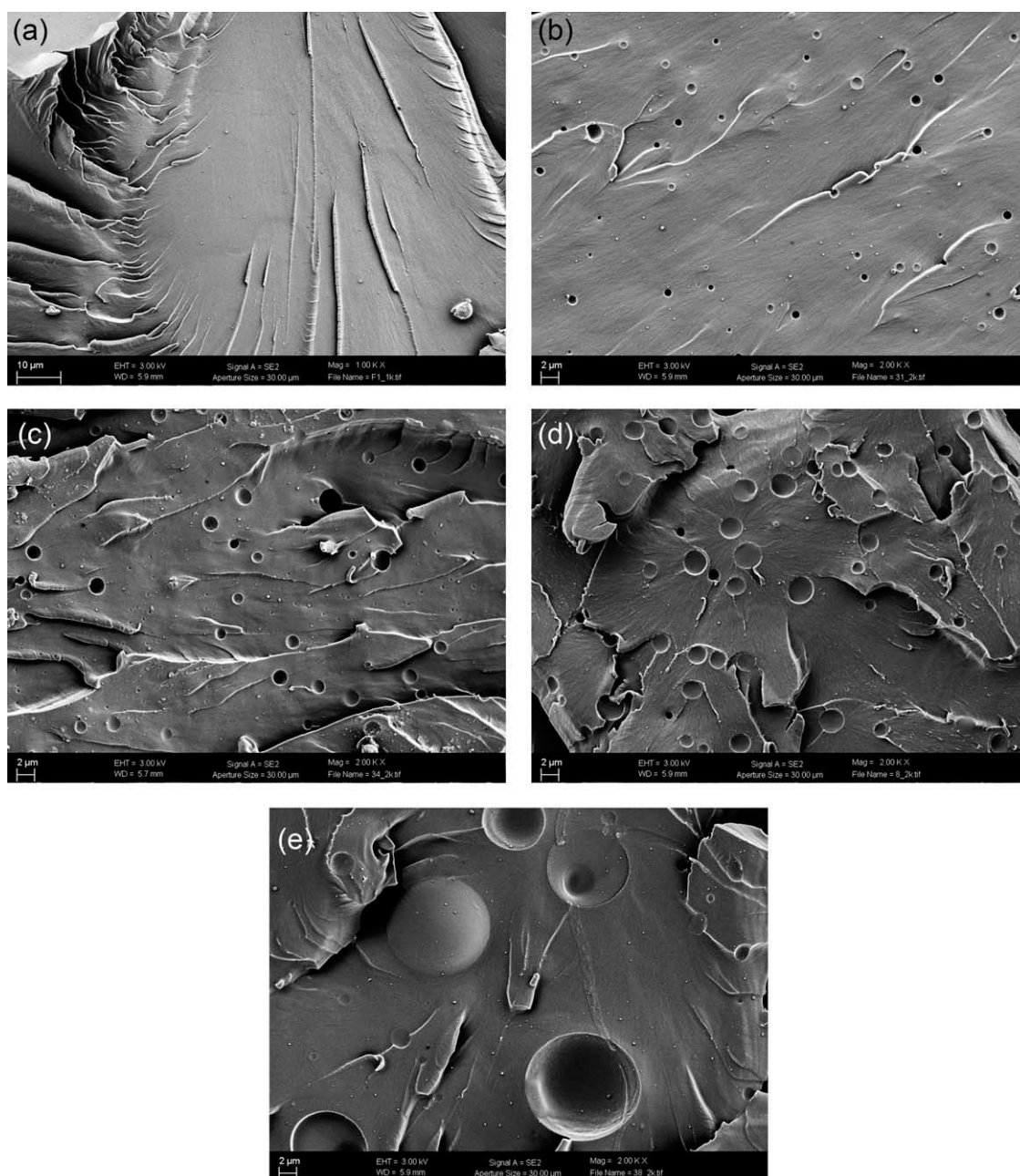
## EXPERIMENTAL METHODS

### Scanning electron microscopy

The fractured surface of modified and unmodified epoxy resin was analysed by Scanning electron microscopy. The fractured surface was coated with a thin layer of gold using a high vacuum gold sputter in a JEOL – JFC -1200 fine coater. A low voltage SEM JEOL, JSM 5600 LV was used to examine the fracture surfaces.

### Dynamic mechanical analysis

Dynamic mechanical measurements were performed from –100 to 200°C at a frequency of 10 Hz and a



**Figure 1** SEM micrographs of (a) Neat epoxy, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt %.

heating rate of 3°C/min using a DMA Q 800 equipped with a three-point bending device with a 44 mm span. Specimens used for dynamic mechanical tests were machined to 60 × 12 × 10 mm from the above plates.

#### Fracture toughness and fracture energy

Fracture toughness of the specimens was determined according to ASTM STP410. Rectangular specimens of 100 mm length, 35 mm width, and 3 mm thickness were used for fracture toughness measurements. A notch of 5 mm was made at one edge of the specimen. A natural crack was made by pressing a fresh

razor blade into the notch. Fracture toughness ( $K_{IC}$ ) values were determined with precracked, single-edge-notched specimens in a three-point bending with a span of 50 mm. The analysis was done in tension mode at room temperature using UTM - FIE tensile testing machine type at a crosshead speed of 5 mm/min, at room temperature.  $K_{IC}$  was determined according to the following relationship

$$K_{IC} = 3PSa^{1/2}Y/2tw^2 \quad (1)$$

where  $P$  is the critical load for crack propagation (in Newtons),  $S$  is the length of the span (in mm),  $a$  is the crack length (in mm),  $t$  is the thickness in mm

**TABLE II**  
The Number Average Diameter of HTLNR Domains in the Modified Epoxy Blend

HTLNR content (wt %)	Dn ( $\mu\text{m}$ )
5	1
10	3
15	6
20	9

and  $w$  is the width in mm.  $Y$  is a geometrical factor given by

$$Y = 1.93 - 3.07 (a/w) + 14.53 (a/w)^2 - 25.4 (a/w)^3 + 25.8 (a/w)^4 \quad (2)$$

### Impact strength

The Izod impact test was performed according to Impact tester of speed 3.46 m/s. and hammer length 0.33 m, at room temperature, according to ASTM D256. The specimen size was  $60 \times 12 \times 3 \text{ mm}^3$ .

## RESULTS AND DISCUSSION

### Morphology of the blends

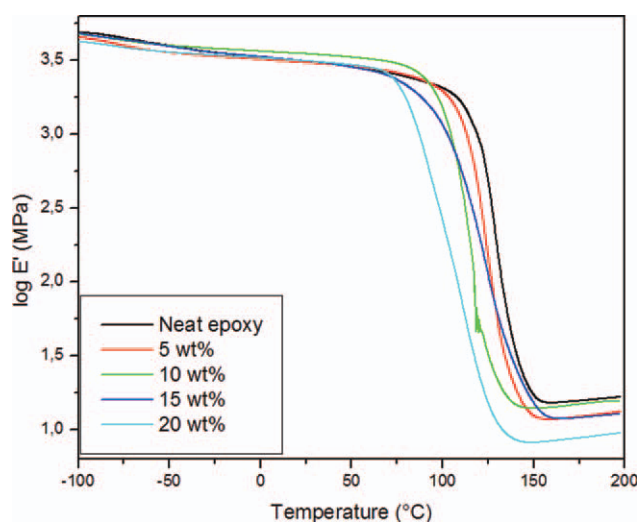
It is important to mention that before crosslinking, the blends had a homogeneous morphology which up on crosslinking underwent reaction induced phase separation (RIPS) process by a nucleation and growth mechanism. SEM micrograph of the fractured surface of the unmodified epoxy system [Fig. 1(a)] shows a smooth glassy fracture surface with cracks in different planes indicating brittle fracture. Unlike the neat epoxy, fracture surface of the rubber-modified ones are rough indicating massive shear deformation. Figure 1(b) represents the modified epoxy sample with 5 wt % HTLNR-epoxy. Here rubber domains appear as small spheres of size  $1 \mu\text{m}$  in the epoxy matrix. The SEM micrographs at higher rubber content exhibit similar matrix droplet morphology and are given in Figure 1(c-e), however the particle size increased with increase in rubber content due to the coalescence process. The rubber domain size at different rubber content is reported in Table II.

### Dynamic mechanical analysis

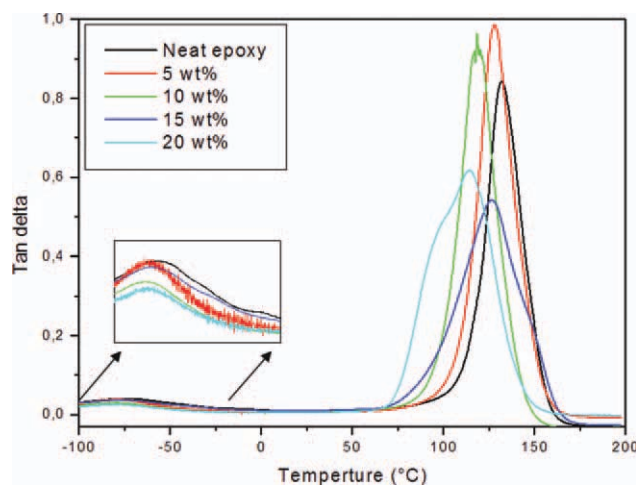
The viscoelastic properties of the blends were studied using DMA. The variation of  $\log E'$  (log storage modulus) with respect to temperature was recorded in Figure 2. The unmodified cross-linked epoxy resin as well as the cross-linked epoxy blend show only one inflection point, at the  $T_g$  of the cross-linked epoxy resin. The  $\log E'$  decreases with an increase in

temperature. The  $\log E'$  of the blends remains same to that of the unmodified epoxy network until the  $T_g$  of the epoxy phase. A sharp decrease in the  $\log E'$  was observed for all blends near the glass transition of the epoxy network; the values thereafter remained constant in the rubbery plateau region, which is typical for cross-linked polymers.<sup>22</sup> It is interesting to note that the  $T_g$  of epoxy rich phase slightly shifts towards the low temperature side with the addition of HTLNR. The decrease in  $T_g$  of epoxy rich phase may be due to the dilution effect by the addition of HTLNR or due to the presence of miscible HTLNR in the epoxy phase and will result in an incomplete crosslinking. The  $\log E'$  of the blends in the rubbery region was slightly less than the neat epoxy system. Also,  $\log E'$  in the rubbery region is an indirect measure of crosslink density. The lower value of  $\log E'$  in this region indicates that the crosslink density of the blends is lower, supporting the above statement.

The plot of  $\tan \delta$  versus temperature is shown for blends in Figure 3. A single relaxation was observed for the unmodified epoxy network and for the blends. The relaxation peak around  $130^\circ\text{C}$  corresponds to the  $T_g$  of the epoxy-rich phase. Careful examination of the  $\tan \delta$  curve of the unmodified epoxy network and the cross-linked epoxy blends reveals a relaxation peak of very low amplitude at around  $-65^\circ\text{C}$  (called  $\beta$  relaxation). This  $\beta$  relaxation is attributed to the motions of glycidyl units in the network.<sup>22</sup> The  $T_g$  of the rubbery phase seems to be overlapped with  $\beta$  relaxation. It is interesting to note that the  $T_g$  of the epoxy-rich phase slightly shifts toward the low-temperature side with the addition of the rubber. As mentioned above the decrease in  $T_g$  of the epoxy-rich phase may be the dilution effect by the addition of the rubber phase, and may also result from the miscible rubber phase in the epoxy



**Figure 2** Variation of  $\log E'$  with respect to temperature for HTLNR modified epoxy. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



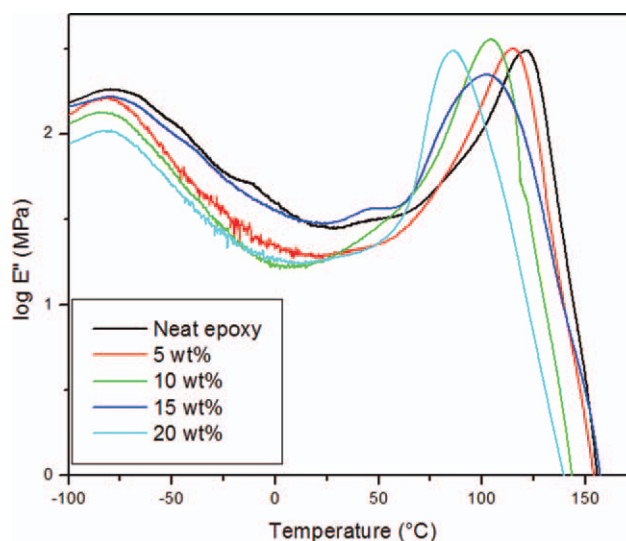
**Figure 3** Variation of Tan delta with respect to temperature for HTLNR modified epoxy. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

rich phase. In addition, the samples with 15 and 20 wt % HTLNR, show two peaks in the  $\tan \delta$  at the  $T_g$  of the epoxy phase, indicating the presence of a lower temperature glass transition, beside the main transition at the same temperature as the crosslinked neat epoxy resin. The presence of a secondary peak, at a lower temperature in the  $\tan \delta$ , suggests the presence of a fraction of IPN type of sponge type structure consisting of miscible epoxy/rubber phase with higher mobility due to a different degree of crosslinking. We believe that this anomalous behavior could be due to the increase in the relative amount of dissolved rubber as rubber content increases and hence having secondary peak at a lower glass transition temperature, as shown in Figure 3. The  $\tan \delta$  peak height, peak area, and peak width are summarized in Table III. Interestingly the  $\tan \delta$  peak height for 15 and 20 wt % HTLNR is lower than the other blends and neat crosslinked epoxy due to the formation of agglomerated subparticles of epoxy phase in the HTLNR droplets, which may enhance the stiffness of the material. The increased peak area and peak width shows better miscibility at higher HTLNR loading.

The molecular weight between the cross-links ( $M_c$ ), which is an indirect measure of cross-link

**TABLE III**  
Parameters Obtained from  $\tan \delta$  Profile

HTLNR content (wt %)	Peak heights	Peak widths	Peak areas	Peak at °C	$M_c$ (g/mol)	$\nu_e \times 10^{27}$ chains/m <sup>3</sup>
0	0.84	22.2	24.66	131	71	10.1
5	0.98	22.84	29.01	127	76	9.4
10	0.96	22.24	25.62	118	92	7.8
15	0.54	39.01	25.36	126	78	9.2
20	0.62	42.59	28.17	114	103	7



**Figure 4** Variation of  $\log E''$  with respect to temperature for HTLNR modified epoxy. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

density of epoxy resin, can be calculated from the  $T_g$  of epoxy rich phase using the following equation.<sup>23</sup>

$$M_c = \frac{3.9 \times 10^4}{T_g - T_{g0}} \quad (3)$$

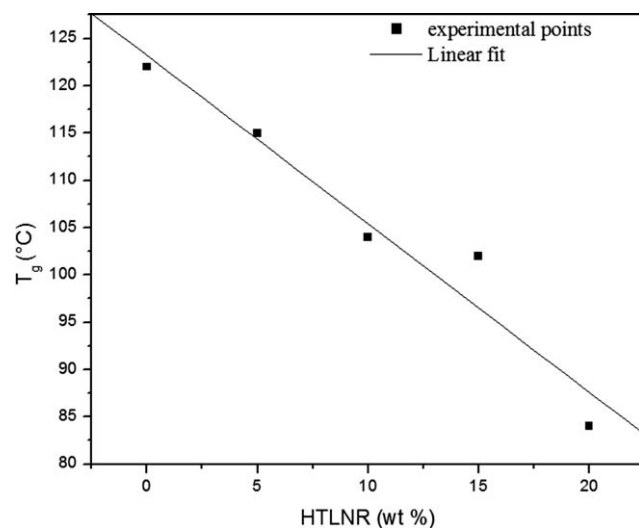
where,  $T_g$  is the glass transition temperature of the cross-linked epoxy resin and  $T_{g0}$  is the glass transition temperature of uncrosslinked polymer having same composition as cross-linked polymer. The value of  $T_{g0}$  was taken as 76°C for DGEBA/DDM system.<sup>24</sup> The effective crosslink density ( $\nu_e$ ) was calculated from  $M_c$  using the following equation.<sup>23</sup>

$$\nu_e = \frac{\rho N_A}{M_c} \quad (4)$$

where,  $\rho$  is the density and  $N_A$  is Avogadro's number.

The molecular weight between the cross links ( $M_c$ ) and the effective cross-link density ( $\nu_e$ ) are summarized in Table III. The increase in  $M_c$  and consequent decrease in cross-link density is evident from the table.

The plot of the  $\log E''$  ( $\log$  loss modulus) as a function of temperature is shown in Figure 4. The  $\log E''$  of cross-linked blends are lower than that of the unmodified epoxy network. The lower values of the  $\log E''$  of the cross-linked blends shows the flexibility of the blends. These results clearly indicate that the addition of HTLNR in epoxy system increases the flexibility of the cross linked epoxy system; this behavior is favorable for the ability of the matrix to deform under shear.<sup>25</sup> Two relaxation peaks are observed in the  $\log E''$  curves. The peak at around 130 °C is due to the epoxy-rich phase, and a  $\beta$  relaxation peak at around -65°C supports the



**Figure 5**  $T_g$  of the epoxy phase with respect to HTLNR component.

results of the  $\tan \delta$  curve. However, a careful examination of loss modulus curves reveals a peak around 60°C called the  $\omega$  relaxation peak due to the lower cross-link density sites in the epoxy network or due to the relaxation overtones in the regions of higher cross-link density matrix which are occluded in the lower cross-link density matrix.<sup>22</sup> The variation of  $T_g$  of the epoxy-rich phase from the  $\log E''$  profile with respect to rubber content is shown in Figure 5. From the Figure  $T_g$  of the epoxy-rich phase shifts towards the low-temperature side with the addition of the rubber as observed in  $\log E'$  and  $\tan \delta$  profiles.

### Mechanical properties

#### Fracture toughness

The fracture behavior of the samples, both HTLNR modified and unmodified were studied. The fracture toughness of 0.85 MN/m<sup>3/2</sup> for neat epoxy system is comparable with the literature values.<sup>25,26</sup> The fracture toughness was found to increase with increase in rubber content as shown in the Figure 6. A dramatic increase in fracture toughness by the addition of rubber particles have been observed, a maximum of around 100% increase was observed for 20 wt % HTLNR modified blends. This is associated with the rubber particles dispersed in the epoxy matrix, which can increase fracture toughness by cavitation and shear deformation in the matrix.<sup>13,27-29</sup>

#### Impact strength

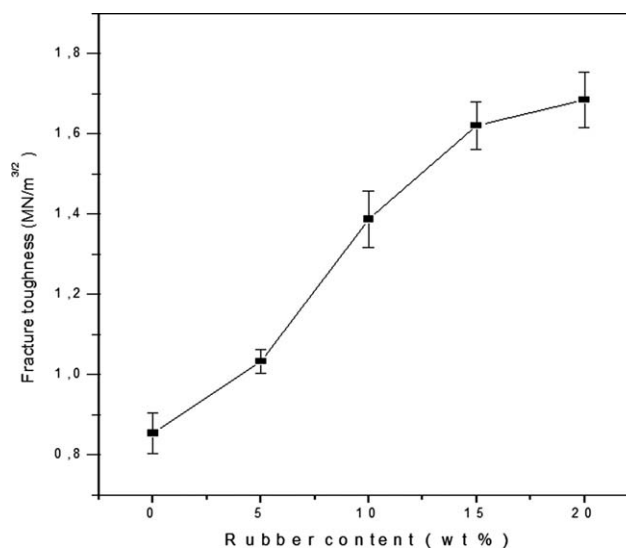
Impact strength is the resistance to sudden shock. It is the energy required to break the sample. For the unmodified samples, the impact strength is low since they are hard and brittle. There is steady increase in the impact strength for the modified

samples. The impact property was enhanced in the case of HTLNR modified epoxy samples with increase in HTLNR concentration up to 15 wt % followed by a decrease. The maximum impact strength of 19.215 kJ/m<sup>2</sup> was obtained at 15 wt % of HTLNR concentration, using unnotched sample [Fig. 7(a)], which is about 100% higher than the neat epoxy; this could be due to greater compatibility of rubber with epoxy resin. Similarly the work done by Ratna,<sup>30</sup> using another rubber carboxyl terminated poly(2-ethyl hexyl acrylate) rubber (CTPEHA) to modify an epoxy matrix, a 60% improvement in impact property was reported. It is well established that rubber particles dispersed in the epoxy matrix increases the impact resistance by shear deformation in the epoxy matrix.<sup>12,13,28,29</sup> However, the impact strength decreases at 20 wt % HTLNR since with increase of the HTLNR loadings, more and more interfaces and interstices are formed, which will deteriorate the mechanical properties of the blends.

The variation of impact strength of unnotched and notched samples are plotted as a function of rubber content in Figure 7(a,b). The unnotched samples are found to have higher impact strength than notched ones since some energy is required to initiate a crack and crack propagation. With increase in rubber concentration the impact strength found to increase. The improvement in impact as a function of composition indicates that the morphology plays an important role in the toughening of the crosslinked epoxy systems.

#### Discussion on toughness

Heterogeneous morphology and good interfacial adhesion between two phases are the most important



**Figure 6** Variation of Fracture toughness with rubber content.

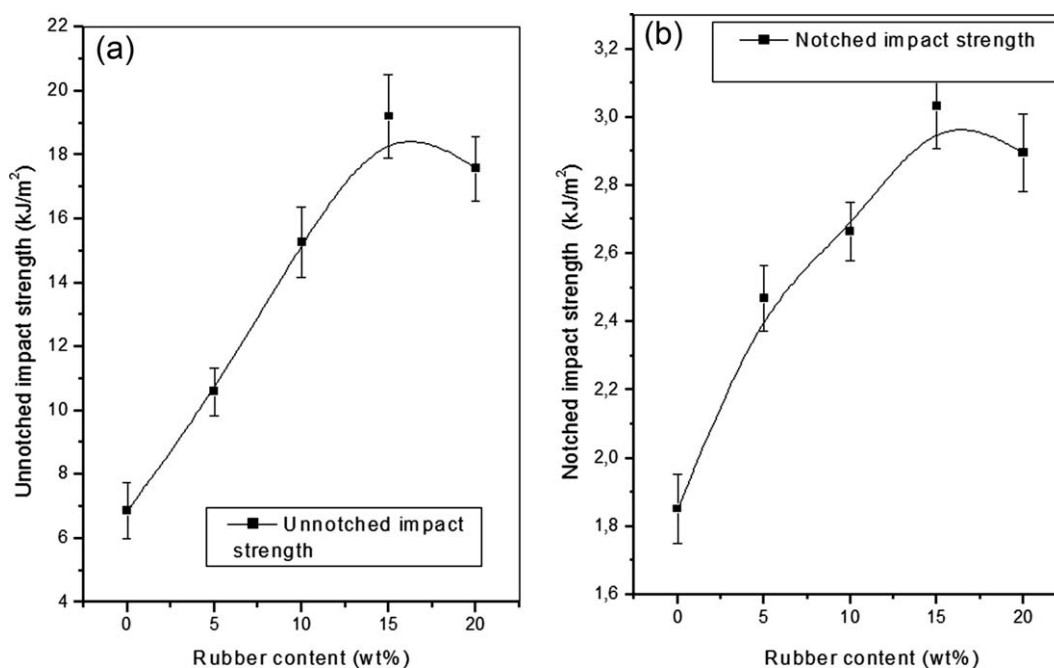


Figure 7 Variation of (a) Impact strength (Unnotched) and (b) Impact strength (Notched) with rubber content.

parameters for obtaining increased fracture toughness in rubber modified epoxy systems. All the blends in this study are heterogeneous and thus satisfy one of the important conditions for improved fracture toughness (Fig. 1). For neat epoxy system, the fracture surface is very smooth and the cracks spread freely and regularly, and oriented in the direction of loading, suggesting typical characteristics of brittle fracture [Fig. 1(a)]. The SEM micrographs of the fracture surfaces of the cured blends containing 5 to 20 wt % HTLNR [Fig. 1(b–d)] clearly show white ring marks around the domains; this is because the dispersed rubber particles act as stress concentrators upon the application of external load and this lead to plastic deformation of the matrix surrounding the rubber particles.<sup>31,32</sup> This will contribute to river marks and hence offer more roughness to the fracture surface. The high degree of roughness on the fractured surface also indicates the crack deviation from its original plane, resulting in an increased surface area of the crack, which also increase the toughness.<sup>33</sup> Moreover, the interface between the epoxy phase and rubber phase remains intact. This is an evidence for good adhesion between the matrix and dispersed domains. Hence, the stress is transferred more effectively to the rubber domains from the cross-linked epoxy phase.

The application of external load may led to cavitation inside the rubber particles; the formation of cavities in the rubber particles elevates the fracture toughness through lowering the local yield stress and provokes extensive shear yielding.<sup>12,13</sup> Shear yielding of the matrix could be another reason for

the increase in toughness. By the application of the load the rubber particle will produce sufficient triaxial tension in the matrix so as to increase the local free volume and hence enabled extensive shear yielding of the matrix.<sup>34</sup> Moreover the rubber particle is considered to bridge the crack as it propagates through the material.<sup>8</sup> Thus, the rubber particles were able to prevent the crack growing to a catastrophic size. The increase in toughness was due to the amount of elastic energy stored in the rubber particles during stretching. Thus, the deformation of the rubber particles in the matrix could be responsible for the enhanced stress transfer and hence the toughness.<sup>20</sup> From our experimental observations, we have maximum improvement in toughness for the 20 wt % HTLNR modified blends. On the other hand, impact strength was highest 15 wt % HTLNR content, this indicate that the cured resin containing HTLNR ranging in between 15 and 20 wt % showed the best balance of properties.

## CONCLUSION

Toughening epoxy resins with functionalized reactive liquid rubbers has been a subject of interest for many investigators. The initial homogeneous blend phase separate through nucleation and growth resulting in final secondary phase separation. The domain size increases with HTLNR content in the blends due to coalescence. For the modified specimens the impact strength (both notched and unnotched) and fracture toughness are found to be

greater than for unmodified epoxy. The HTLNR droplets act as stress concentrators leading to the plastic deformation in the surrounding matrix may take up a significant amount of applied stress. Cured epoxy resin containing HTLNR ranging in between 15 and 20 wt % showed the best balance of properties.

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