Chapter 3

Miscibility, Phase Behavior and Morphological Characteristics of Rubber-Modified Epoxies

The chapter discusses the miscibility aspects and phase separation behavior of epoxy-elastomer blends with varying weight contents of the elastomer. The demixing phenomenon and in-situ phase growth of epoxy-CTBN blends were analyzed by Small Angle Laser Light Scattering (SALLS), Optical Microscopy (OM), and Scanning Electron Microscopy (SEM). Phase diagram has been computed based on interaction parameters from the Flory-Huggins equation on free energy of mixing. Finally, the developed morphology of the cured blends was analyzed using SEM and Atomic force microscopy (AFM). Toughening mechanism prevailing in elastomer-modified epoxy blends were also discussed based on the developed morphology.

Parts of the results of this chapter

i. have been published in Journal of Polymer Science Part B: Polymer Physics 2004, 42, 722.

ii. have been submitted for publication in J Phy Chem B
Generally, epoxy-hardener-elastomer system is homogeneous in the initial state or becomes homogeneous at a slightly higher temperature than the room temperature. During the course of the cure reaction via liquid-liquid phase separation, the increase of the average molar mass of the polymerizing components causes poor miscibility between the rubber and the epoxy and finally forms regular phase separated morphology. This is termed, generally, as reaction induced phase separation (RIPS) phenomenon. Also, because of chemical modifications, there are variations in the interaction between the components during conversion. These collective changes force the system to cross thermodynamic phase boundaries so that the system transforms from a homogeneous state to micro-phase separated one. The final morphology of the system depends on the kinetic competition between phase separated rates, reaction rates and the connectivity between the phases. Several two-phase structures are developed during the course of the conversion, such as, co-continuous structures, uniform spherical domain structures, and bimodal spherical domain structures. Thus during the RIPS process, the system may force to pass through all these morphological states which are controlled by the rate of reaction and phase separation (PS).

The PS or demixing phenomenon in thermoset-rubber blends have received much attention and have been discussed in literature due to its unusual equilibrium and non-equilibrium pattern formations [1-4]. When a homogenous reactive polymer blend was lifted to an unstable spinodal region, various modes of concentration fluctuations developed. A nucleation and growth (NG) mechanism may take place in RIPS simultaneously with spinodal decomposition (SD). Yamanaka et al. [5] have reported the curing induced PS of elastomer-epoxy blends via SD. Phase separation by NG mechanism is also expected to occur, since during cure, the system has to pass through the metastable region before
it is thrust into an unstable region. But, NG is expected to be a slow process with the development of any elastomer domains with well-defined correlation length and hence unable to show a light-scattering peak. Thus the region may be skipped. However, it has been proved that NG happens in polymerization induced phase separation (PIPS) of certain elastomer-modified epoxies [6-7]. Also, it has been proved that the real phase separation via NG mechanism takes place well before the cloud point (CP) temperature determined by light scattering (LS) technique.

The theoretical backgrounds of Phase separation process have been explained elsewhere [8]. The mechanism of PS, whether NG or SD, was determined by the composition and curing temperature [9-26]. The mechanism, in turn, determines the morphology and the mechanical properties of the product. Verchere et al. [27] reported that low values of interfacial tension and polymerization rates favor NG in most cases. Still in certain other studies, phase separation based on SD has been observed and explained based on LS analysis for various rubbers and thermoplastic additives [5, 28-31]. Chen et al. [6] employed small angle X-ray scattering (SAXS) to study the real beginning of PS mechanism in CTBN-modified epoxies cured with amine hardener and observed to be taking place before the onset of PS as determined by LS. Okada [7] and co-workers have studied PS induced by chain polymerization of 2-chloro styrene in a polystyrene/dibutyl phthalate mixture followed by a time-resolved LS technique and SEM.

Phase behavior and separation dynamics have been studied [32] in amine cured epoxy resin using reactive liquid rubber through application of DSC, one- and two-dimensional light scattering and OM. Phase separation behavior analyses have been reported in thermoplastic/thermosetting polymer blends using light scattering experiments [33]. Phase separation mechanisms and the probing methodologies [34-35] are well documented.
Recently, reaction-induced microphase separation has been studied [36-37] in epoxy resin with new block copolymers. The effect of topological structures of block copolymers on the morphological structures of the thermosets was investigated. l'Abee et al. [38] have reported on reaction-induced phase separation (RIPS) of thermoplastic vulcanizates (TPVs) with fine rubber dispersions. Scanning electron microscopy confirmed the formation of cross-linked rubber particles. The morphology development during phase separation was studied by optical microscopy and time-resolved small-angle light scattering (SALS). Polymerization induced phase separation phenomenon has been studied in PMMA–epoxy–clay ternary composites [39]. Transmission electron microscopy (TEM) analysis showed that phase separation between PMMA and epoxy network was obtained in the form of spherical nodules. Wide-angle-X-ray (WAXS) and small angle X-ray scattering (SAXS) were used for the investigation.

In an interesting study by Gomez et al. [40], the cloud point temperatures and phase diagrams of four series of epoxy/polystyrene blends have been determined. The phase diagrams showed UCST behaviour. The Flory–Huggins theory with a concentration-dependent interaction parameter has been developed to study the compatibility of two polymers in presence of spherical nanoparticles. Dean et al. [41] have performed dynamic mechanical thermal analysis and small angle neutron scattering (SANS) on a number of methacrylate /epoxy interpenetrating polymer networks (IPNs) and semi-IPNs to probe their phase structure. DMTA analysis of the rubbery region of the semi-IPNs revealed that they had either a co-continuous morphology or a matrix phase that was cross-linked.

The chapter discusses the RIPS behavior in CTBN-modified bisphenol-A based epoxy systems cured using an anhydride hardener. Most of the phase separation studies of epoxy-CTBN systems were cured using amine hardeners. In the present study, an anhydride is used as the curative. This
keeps the system and the study unique. The curing was monitored in-situ using various observation techniques to analyze the phase growth and the resultant morphological evolution. The development of PS and particle growth during the demixing process were studied using small angle laser light scattering (SALLS) and morphological changes by optical microscopy (OM) and techniques such as SEM and atomic force microscopy (AFM). SEM has been used to study the phase separation behavior at different stages of cure to get direct representations. Since HTPB is immiscible in epoxy resin, SALLS technique has no scope in the phase behavior study. However, morphology analyses by SEM and AFM have been employed in the study.

3.1 Small angle laser light scattering (SALLS) studies
Dynamic as well as isothermal light scattering studies have been performed on epoxy-CTBN blends having different weight contents of elastomer so as to analyze the phase growth behavior during the cure reaction.

3.1.1 Epoxy-CTBN (5 phr) blend
The dynamic light scattering measurements of epoxy-5 phr CTBN blend have been done to obtain the miscibility as well as the cloud point temperatures and the scattering profiles are depicted in Fig.3.1. Fig. 3.1(a) and (b) represent the scattering profile at scattering angles of 5.51 and 10.31 respectively. Particles that are present initially in the system causes scattering of light. As temperature increases, the particles go into the resin system which causes decrease in intensity of scattered light to the base plateau region. Thus, an upper critical solution temperature (UCST) behavior is noted. As temperature increases further, particles develop due to demixing phenomenon which again leads to increase in intensity of scattered light. The UCST point and initiation of demixing process are represented by arrows A and B in Fig. 3.1 (a) and 3.1 (b). These points were near about 40 and 69°C respectively and did not differ much with respect to the scattering angle.
Figure 3.1: (a) Dynamic light scattering profile of epoxy-CTBN (5 phr) blend at a scattering angle of 5.51

Figure 3.1: (b) Dynamic light scattering profile of epoxy-CTBN (5 phr) blend at a scattering angle of 10.31

Fig. 3.1 (c) compares the correlation length of the developing network, based on the data obtained from dynamic measurements, even though the values are not absolute. The correlation length, represented by arbitrary scale of unit, denotes the distance between the phase separated particles and was computed from the slope ($S$) and intercept ($A$) of the curve.
\( \frac{1}{\sqrt{I}} \) versus \( q^2 \) where \( I \) denotes intensity and \( q \) signifies scattering vector. The correlation length (\( \xi \)) was calculated as \( \xi = \frac{S}{A} \). The values increased as temperature increased, as observed from the results. For 5 phr CTBN-epoxy blend system, the average values were 0.46, 0.61 and 0.93 µm at temperatures 70, 80 and 90°C respectively.

**Figure 3.1: (c)** Dynamic light scattering profile of epoxy-CTBN (5 phr) blend: \( \frac{1}{\sqrt{I}} \) versus \( q^2 \)
Figure 3.2: (a) Isothermal light scattering profiles of epoxy-CTBN (5 phr) blend system, $T_{\text{cure}} = 100^\circ\text{C}$

Figure 3.2: (b) Isothermal light scattering profiles of epoxy-CTBN (5 phr) blend system, $T_{\text{cure}} = 120^\circ\text{C}$
Fig. 3.2 (a) and (b) are scattering profiles of the system during isothermal curing at 100 and 120°C respectively. The particle growth was registered a little early at 120°C compared to the curing at 100°C, displaying the curing reaction as a thermally catalyzed one. The scattering profile reflects the evolution of particles during the demixing phenomenon. The scattering of light is partly governed by chemical kinetics and hence the pattern of light intensity profile, especially intensity, will vary with temperature difference. The shift in the peak intensity towards lower angles, as demixing proceeds, is evident from the Figures (the arrows denote the shift). This pattern of scattering profile is considered as evidence for SD mechanism.

Thus, with some evidence, the SD demixing mechanism can be confirmed from the scattering profile. Further, the morphological pattern of the developing particles by optical microscopy showed bi-continuous structures before forming final phase separated structures.

Fig. 3.2 (c) [i, ii, iii and iv] depict the OM images of the developed structures, at 120°C cure, during the phase separation phenomenon. The enlarged images are shown so as to view the small dispersed particles. Fig. 3.2 (c) [i] shows the very small dispersed particles of CTBN in epoxy resin at the initial stage of mixing. These dispersed particles before the start of the reaction shows partial miscibility of the elastomer in the epoxy matrix. During curing as temperature increased, the elastomer particles got dissolved into the resin to form homogeneous blend. Fig. 3.2 (c) [ii] depicts this. No particles were observed in the system. As a result of demixing phenomenon, during curing, bi-continuous structural evolutions, which seemed unstable, constantly changing and resembling SD, were observed. This occurred after 12.5 min of cure process. Since these transformations occurred very rapidly with short time scales, I could hardly present all the emerging structures. This dynamic and unstable state which showed morphological variations with conditions is represented in Fig. 3.2 (c) [iii]. This is reminiscent of the system in the
metastable state of the phase diagram presented in this chapter [Fig. 3.16]. In the metastable state, the particles are stable only at defined conditions. However, as conditions vary (this happens because the system is dynamic), the structures change to a number of metastable structures, before attaining the ultimate morphology. Finally, the structures assume particle-matrix bimodal morphology denoted by [iv]. The dispersed particles are well obvious in the image. It is generally accepted that the structure fixation at the early stage of SD should yield the bi-continuous two-phase structure which is characteristic of SD. This is a supplementary evidence for the structure development mechanism via SD.

Fig.3.2: (c) [i]
Fig. 3.2: (c) [ii]

Fig. 3.2: (c) [iii]
Figure 3.2: (c) [iv] OM images during cure of epoxy-CTBN (5 phr) blend at 120°C isothermal cure

The morphological development of the particles was well observed by SEM analysis of the cured sample. Fig. 3.2 (d) [i and ii] represents the SEM images of the cured sample. The images are magnified at different levels, i.e. 500 x and 1000 x. Phase separated particles are observed inside the circle on the images.

(i) 500 x  
(ii) 1000 x  

Figure 3.2: (d) [i and ii] SEM images of epoxy-CTBN (5-phr) blend at 120°C isothermal cure
Now it is significant to analyze the linearized theory of Cahn-Hilliard [42] to the early stage of the demixing process. The isothermal scattering profile of 5 phr CTBN system, as an example for in the present case, one can observe no scattering peak in the early stage of the reaction, within the scattering vector range studied. The initial decrease in the scattering intensity was due to the miscibility of the rubber in epoxy. The dispersed rubber particles got dissolved in epoxy at its miscibility temperature, and formed a homogeneous solution. This was an instant just before the initiation of the reaction. As demixing process initiated, the intensity of the peak increased slowly and then shot up rapidly. After it reached the maximum, the intensity slowed down and became approximately constant. At this time, the phase separated domains attained a constant state with no further increase in size. Additional increase in the micro phase separation and particle growth became arrested quickly at this stage due to the transformation of the system to a vitrified nature. The scattered peak appeared to be quite broad due to the large distribution of inter domain spacing. The development of the total scattered intensity or invariant, $Q$, can be related to the onset of micro-phase separation during the demixing process. The invariant is independent of the size or the special arrangement of the structural inhomogeneities and is expressed as:

$$Q = \int I(q) q^2 dq \phi (1 - \phi) (\Delta n)^2 \quad \text{(3.1)}$$

where

$$q = \frac{4 \pi n}{\lambda} \sin \left(\frac{\theta}{2}\right)$$

$\phi = \text{Volume fraction of CTBN-rich phase}$

$\Delta n = n_{\text{CTBN}} - n_{\text{epoxy}}$ is the difference in refractive index of the two phases.

$\lambda = \text{wavelength of light}$

$\theta = \text{scattering angle measured in the medium}$
The invariant \( Q \) was employed to characterize the structure development as well as the degree of phase separation. The increase in \( Q \) corresponds to an increase in the degree of phase separation and gives a quantitative indication of the fluctuation in the growth of the phase separated particles.

As the polymerization reaction continues, the degree of polymerization of elastomer domains i.e. the quench depth continues to increase. Unlike in non-reactive binary blends, in reactive blends the quench depth increases continuously as the reaction progresses, because the polymer molecular weight increases and the isoquench conditions are lost. Depending upon the quench depth, the mixture can phase separate by either NG or SD mechanism. In CTBN-epoxy blend system, the formation of non-equilibrium bi-continuous structures at the beginning of phase separation was observed. These highly inter-connected structures confirm the mechanism as SD. The scattering maximum also showed a peculiar characteristic where it first appeared at a large wave number, and the peak position remained virtually invariant for a short period. It means the peak showed little or no movement. At a latter time, the peak was shifted to lower wave numbers due to phase growth. This means that the phase movement at the early stage of SD was so small so much so that it may be worthy of testing with the linearized theory of Cahn-Hilliard [42], which predicts an exponential growth of a scattering function as per the expression:

\[
I(q, t) = I(q, t = 0) \exp\left[2R(q)\right]t \quad \text{-------- (3.2)}
\]

where \( t \) is the phase separation time.

\( q \) is the scattering wave number defined previously under the expression (3.1)

\( R(q) \) denotes the amplification factor which represents the growth of composition fluctuations [43-44] of the mixture and depends on \( q \).
Therefore a plot of \( I(q) \) versus \( t \) (Fig 3.3) should be a straight line during the early stage of phase separation. \( R(q) \) is expressed as:

\[
R(q) = -Mq^2 \left\{ \frac{\partial^2 f}{\partial c^2} + 2\kappa q^2 \right\}
\]

where \( f \) the local free energy density of the homogeneous system is, \( c \) is the concentration, \( \kappa \) is an energy gradient coefficient, and \( M \) is a translational diffusion coefficient.

The strong peak in the scattering profiles suggests that the phase separation proceeded via a SD mechanism [45]. Even though the reaction–induced spinodal decomposition is different from isothermal decomposition, it is reasonable and interesting to check the validity of Cahn-Hilliard theory during the early stage of phase separation.

**Figure 3.3:** Plot of \( I(q) \) as a function of time for epoxy-CTBN blend system
It is obvious that there exists a good fit of the $\ln I(q,t)$ data to a straight line after the onset of phase separation. The values of $R(q)$ were calculated from the slopes of the $\ln I(q,t)$ vs. $t$ curves and taken as half of the value of the gradient. $R(q)$ is the rate at which the amplitude and $q$ varies, and a linear relationship between $R(q)/q^2$ and $q^2$ was predicted from the theory of Cahn and Hilliard. The values are plotted in Fig. 3.4. The data can be approximated fairly well by linear slopes, except for few points at low $q$. It should be pointed out that these data at low $q$ were somewhat affected by the parasitic scattering arising from the beam stop.

![Figure 3.4: Cahn-Hilliard’s plot of $R(q)/q^2$ versus $q^2$ for different temperatures](image)

The validity of the linearized theory for the early stage of spinodal decomposition has been tested by many investigators. Hashimoto and co-
workers [46-47] were the first to show experimentally that there is an appreciable period where the scattering peak is invariant and $R(q)/q^2$ versus $q^2$ plots give linear slopes. Okada and Han [48] also observed the linear regime in the early stage of SD for polystyrene (PS)/poly (vinyl methyl ether) (PVME) blends. An almost similar result for polycarbonate (PC)/poly (methyl methacrylate) (PMMA) mixtures was also reported [49]. Later, Bates [50] was able to show the applicability of this theory even if the time evolution of the structure function is weakly nonlinear i.e. the scattering peak shows a very small movement. Oono and Puri [51] were able to predict the existence of a linear region in binary mixtures based on cell dynamics.

3.1.2 Epoxy-CTBN (10 phr) blend

The dynamic light scattering curve of a 10 phr CTBN-epoxy blend system is shown in Fig. 3.5. As explained previously, the rubber is not miscible in the resin, initially. Scattering due to these particles takes place. As temperature progresses, rubber particles become miscible in the resin. This leads to the decrease in intensity of scattering light, denoted by arrow A. At the UCST point the intensity of scattered light become minimum (arrow B). As temperature increases, phase separation initiates, which leads to the development of particles. This again causes variation in intensity of scattering light (represented by arrow E). The state of the system between B and D, which is signified by an arrow C, represents the region of reactive compatibilisation of rubber in epoxy. The intensity remained same as no particle develops in this region. The sharp increase in the intensity of the scattering profile (denoted by E) is due to the reaction induced phase separation. In this scattering profile the scattering angle is 5.88. This type of scattering profiles with deviations is common in SALLS technique. This is due to scattering of light by generated particles in the system. Although the scattering data is quite strong, the profile shows a clear trend. Since the transitions are relatively broad it is impossible to indicate exactly the miscibility and cloud point temperatures. It is to be remembered that the system is with certain molecular weight distribution.
Fractions with a low molecular will behave differently from fractions with a high molecular weight. This scattering profile is included so as to have a clear understanding on the reaction induced phase separation.

Fig. 3.6 (a) and (b), show the scattering profiles at isothermal cure temperatures of 100 and 120°C respectively. In fact, as compared to the 5 phr system, the intensity of particle growth was lesser here at an instant of 1000 s, probably attributed to the dilution effect due to more CTBN content, which caused delay in gelation. This effect has been proved in rheological analysis where delay in attaining complex viscosity was observed in high rubber content epoxies. The intensity variation of the scattering profile clearly indicates the particle growth during the cure reaction. The shift in the intensity peak towards lower angles hints on the spinodal demixing mechanism during curing.
Figure 3.6: (a) Isothermal light scattering profiles of epoxy-CTBN (10 phr) blend system, $T_{\text{cure}} = 100^0\text{C}$

Figure 3.6: (b) Isothermal light scattering profiles of epoxy-CTBN (10 phr) blend system, $T_{\text{cure}} = 120^0\text{C}$
The OM photographs of the same blend system during the course of the reaction at 120°C are depicted below in Fig. 3.6 (c) [i, ii, iii and iv] which represent direct evidence for morphology changes in the system. The very feebly dispersed CTBN particles in the blend system, Fig. 3.6 (c) [i], soon became homogeneous when heated up to the miscibility temperature represented by Fig. 3.6 (c) [ii]. This is reminiscent of the arrow, C, represented in the Fig. 3.5. As cure reaction proceeded, non-equilibrium bi-continuous structures developed after 13.8 min of cure represented by (Fig. 3.6 (c) [iii]). Later, within 1 or 2 min, the bi-continuous structures split up to generate elastomer droplets, dispersed in the epoxy matrix and finally formed phase separated particulate structures. Later there observed a tendency to form larger droplets from smaller ones, what is called ‘Ostwald ripening’. A decrease in the total number of particles was also observed. Finally the morphology got fixed into bimodal particles/matrix structure as demonstrated in (Fig. 3.6 (c) [iv]). The growth of the phase separated particles was represented by the intensity increase in the isothermal scattering profile. In this system, the method of phase separation, at least partially, was supposed to be occurred via NG mechanism.
Fig. 3.6: (c) [I]

Fig. 3.6: (c) [II]
Figure 3.6: (c) [i, ii, iii and iv]  OM images during cure of epoxy- CTBN (10 phr) blend at 120°C isothermal cure
The SEM images of the cured blend sample of different magnifications such as 500 x, 1000 x, 2500 x and 5000 x are represented in Fig. 3.6 (d) [i, ii, iii, iv] respectively. The dispersed elastomeric domains are well observed. At lower magnifications (i.e. 1000 x, 2500 x), circles are drawn to highlight the elastomer domains. The magnified SEM images are sufficiently large and clear, unlike OM pictures, so that dispersed elastomer particulates are well detected.

Figure 3.6: (d) [i, ii, iii and iv] SEM images of epoxy-CTBN (10 phr) blend at 120°C isothermal cure.
Chapter 3

3.1.3 Epoxy-CTBN (15 phr) blend

Fig. 3.7 (a) and (b) are the dynamic light scattering curves, at two different scattering angles. The scattering profile clearly demonstrates the development of phase separated particles due to demixing phenomenon.

Figure 3.7: (a) Dynamic light scattering profile of epoxy- CTBN (15 phr) blend (scattering angle = 5.51)

Figure 3.7: (b) Dynamic light scattering profile of epoxy- CTBN (15 phr) blend (scattering angle = 10.31)
The isothermal light scattering profiles at 100 and 120°C cure temperatures are depicted in Fig. 3.8 (a) and (b). The increase in intensity of scattering profiles indicates the development of phase separated particles. The isothermal curves showed, initially, a peak at large angles which then shifted rapidly towards smaller angles. This is a typical intensity profile of spinodal demixing. As cure reaction proceeded, network formation developed, epoxy became dense and refractive index came closer to that of the elastomer resulting in the decrease of total scattered intensity. On the other hand, elastomer droplets become larger at the expense of smaller droplets as cure proceeded, and are turn out to be too large to contribute to the scattering in the experimental q-windows.

![Figure 3.8: (a)](image)

**Figure 3.8: (a)** Light scattering profiles of epoxy-CTBN (15 phr) blend system, Isothermal $T_{\text{cure}} = 100^\circ\text{C}$
The morphological changes during cure by OM are typical of viscoelastic phase separation and are shown in Fig. 3.8 (c) [i, ii, iii and iv]. The enlarged images are shown so as to observe the developed particles clearly. It is to be noted that the bigger structures are air bubbles and not particles. Fig. 3.8 (c) [i] and [ii] represents homogeneous blend systems. Some particles viewed in the images disappeared as temperature increased. At the start of the spinodal phase separation, at 14th min the amplitude of concentration fluctuation increased and bi-continuous structures were viewed. The micrograph [iii] depicts bi-continuous fluctuating structures, which ultimately developed to well define structures. This is clearly a signature of SD mechanism.
Fig. 3.8: (c) [i]

Fig. 3.8: (c) [ii]
Figure 3.8: (c) [i, ii, iii and iv] OM images during cure of epoxy-CTBN (15 phr) blend at 120°C isothermal cure
The SEM micrographs of the cured sample Fig. 3.8 (d) [i, ii, iii, and iv] show the development of dispersed phase separated elastomeric particles. The images along with their corresponding magnifications are represented below.

(i) 1000 x  
(ii) 2500 x  
(iii) 5000 x  
(iv) 10000 x

**Figure 3.8: (d) [i, ii, iii and iv]** SEM micrographs of epoxy- CTBN (15 phr) blend at isothermal $T_{cure} =120^\circ$C

### 3.1.4 Epoxy-CTBN (20 phr) blend

The dynamic light scattering profile of the blend system is depicted in Fig. 3.9 (a) and (b) at scattering angles 6.25 and 10.31 respectively. The particle growth is well identified. The “shoulder” in curve (a) may be due to some coalescence of particles which was not observed in (b).
Figure 3.9: (a) Dynamic light scattering profile of epoxy- CTBN (20 phr) blend (scattering angle = 6.25)

Figure 3.9: (b) Dynamic light scattering profile of epoxy- CTBN (20 phr) blend (scattering angle = 10.31)

Correlation length, \( \xi \), was estimated for 20 phr CTBN-epoxy systems at three different temperatures from dynamic light scattering data as depicted.
in the Fig. 3.9 (c). The values of  were 1.29, 1.20 and 0.77 µm at 60, 65, 70°C respectively. The values decreased as cure temperature increased. The decrease in the values of  with respect to the increase in temperature implies the formation of more particles as cure reaction proceeds. Gap between the particles decrease as more and more particles are formed.

![Graph](image)

**Figure 3.9: (c)** Dynamic light scattering profile of epoxy-CTBN (20 phr) blend: $1/\sqrt{I}$ versus $q^2$

Fig. 3.10 demonstrates the scattering intensity at different angles as temperature progresses. The Figure demonstrates the growth of phase separated particles during curing. Higher scattering intensity was observed at lower angles indicating the domain growth size. The temperature instant at which phase growth starts is clearly visible in the diagram which is near 100°C.
The isothermal scattering profiles at 100°C of 20 phr CTBN-epoxy blend is represented in Fig.3.11 (a). The increase in intensity indicates large phase separation nature during cure reaction.

Figure 3.11: (a) Light scattering profile of epoxy-CTBN (20 phr) blend system, isothermal $T_{\text{cure}} = 100^\circ$C
The SEM images of the cured samples at this cure temperature showed developed particulate morphology. The micrographs at magnifications, 10000 x and 20000 x, are depicted in Fig. 3.11 (b) [i and ii].

![SEM micrographs](image)

**Figure 3.11 (b):** SEM micrographs of epoxy-CTBN (20 phr) blend at isothermal $T_{cure} = 100^\circ C$

The following Fig. 3.12 (a) represents the LS profile at an isothermal reaction temperature of $120^\circ C$. The peak intensity decreased without a substantial change in position, and finally, the scattering peak disappeared. The OM micrographs during cure at this temperature are depicted in Figs. 3.12 (b) [i, ii, iii, and iv]. The initial immiscible nature of the system is represented by Fig. [i]. Fig. [ii] reflects the initiation of particle growth after passing through the homogeneous state. In fact, the homogeneous state of the system is not represented here. The evolution of morphology was found to be a time-dependent one. Constantly changing bi-continuous type morphology was observed after 16 min followed by the appearance of phase separated elastomers at the onset of phase separation. The phase separated structures showed a reminiscent of spinodal decomposed texture. The final phase separated structure Fig. [iv], showed a bimodal distribution of phase separated particles. The scanning images of the finally cured blend
at magnifications 5000 x, 10000 x and 20000 x are depicted in Figs. 3.12 (c) [i, ii and iii] respectively. A clear phase separation is evident from the LS profile and from the scanning images.

Figure 3.12: (a) Light scattering profiles of epoxy-CTBN (20 phr) blend system, isothermal $T_{\text{cure}} = 120^\circ$C

Fig 3.12: (b) [i]
3.1.5 Epoxy-CTBN (25 phr) blend

The dynamic scattering profile of 25 phr CTBN-epoxy system is depicted in Fig. 3.13 (a) and (b) at different scattering angles, say, 5.88 and 10.68. Also, there observed a linear relation [Fig. 3.13 (c)] in the lower region of the temperature scan. The higher temperature region did not obey a linear
relation, mainly due to multiple scattering due to phase separated domains. Comparative domain correlation length, $\xi$, was estimated from the slope and intercept of the curves. The values were 1.2, 0.83, and 0.80 $\mu$m at temperatures 70, 75 and 80°C respectively. The values decreased with temperature like other systems.

**Figure 3.13:** (a) Dynamic light scattering profile of epoxy-CTBN (25phr) blend at a scattering angle of 5.88

**Figure 3.13:** (b) Dynamic light scattering profile of epoxy-CTBN (25phr) blend at a scattering angle of 10.68
Figure 3.13: (c) \( \frac{1}{\sqrt{T}} \) versus \( q^2 \): Dynamic light scattering profile of epoxy-CTBN (25 phr) blend

The scattering profiles of isothermally cured blends at 100 and 120\(^0\)C are represented by Fig. 3.14 (a) and (b) respectively. An abrupt increase in intensity was noticed for 120\(^0\)C cured sample in a shorter time than that of the sample cured at 100\(^0\)C. This underlines the thermal reaction kinetics.

Figure 3.14: (a) Isothermal light scattering profiles of epoxy-CTBN (25 phr) blend system, \( T_{\text{cure}} = 100^0\)C
Figure 3.14: (b) Isothermal light scattering profiles of epoxy-CTBN (25 phr) blend system, $T_{\text{cure}} = 120^\circ$C

The OM images, Fig. 3.14 (c) [i, ii, iii and iv] during the isothermal cure of the blend at $120^\circ$C showed the progress of the phase separated structures via spinodal like unstable bi-continuous structure development after 17.0 min of curing. The Figure (i) shows initial elastomeric dispersions whereas (ii) represents the initiation of miscibility, even though all elastomeric particles were not fully homogenized with epoxy resin. The Figure (iii) corresponds to the building up of the bi-continuous morphology during cure polymerization via the demixing phenomenon. Numerous instant and unstable structures were emerged rapidly and finally fixed to particle-matrix morphology. Even though, it was difficult to record all instantaneous structural evolutions, Figure (iii) depicts a representative example. Many distorted elastomeric domains were observed which finally attained spherical shape. The ultimate development of phase separated elastomeric dispersions in the matrix epoxy is pictured in (iv) which demonstrates a bimodal morphology.
Figure 3.14: (c) [i, ii, iii and iv] Optical micrographs of epoxy-CTBN (25 phr) blend at isothermal $T_{\text{cure}} = 120^\circ\text{C}$
The SEM images of the cured blend at this cure temperature depicted in Fig. 3.14 (d) [i, ii, iii and iv], showed clear pictures of phase separated domains. The magnifications of the Figures are in the order of 500 x, 1000 x, 2500 x and 5000 x for Figures i, ii, iii and iv respectively.

(i) 500 x  
(ii) 1000 x  
(iii) 2500 x  
(iv) 5000 x  

Figure 3.14: (d) [i, ii, iii and iv] SEM micrographs of epoxy- CTBN (25 phr) blend at isothermal $T_{\text{cure}} = 120^\circ$C

The nature of the evolved light scattering profile in all modified epoxies indicated SD as the prime mechanism. The non equilibrium bi-continuous texture of the developed particles from OM images, further, proved the mechanism.
3.2 Size of phase separated particles

SALLS technique provided the opportunity to compute the size of phase separated elastomeric particles in the matrix epoxy.

From SALLS analysis, the correlation length ($\xi$) was determined from the expression:

$$\xi = \sqrt{\frac{S}{A}}$$ \hspace{1cm} (3.4)

where $S$ is the slope curve and $A$ is the intercept of the curve of $q^2$ vs $\frac{1}{\sqrt{I}}$.

The particle diameter, $d = \frac{6\Phi}{A_0}$ \hspace{1cm} (3.5)

where $\Phi$ stands for volume fraction of the dispersed phase and $A_0$ is the surface area.

$A_0$, in turn, was obtained from volume fraction and correlation length using the following expression:

$$A_0 = \frac{4\Phi(1 - \Phi)}{\xi}$$ \hspace{1cm} (3.6)

The values obtained are furnished in Table 3.1.

**Table 3.1: Particle size- SALLS analysis**

<table>
<thead>
<tr>
<th>Epoxy systems</th>
<th>Particle diameter from light scattering studies ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 CTBN</td>
<td>0.54</td>
</tr>
<tr>
<td>10 CTBN</td>
<td>0.76</td>
</tr>
<tr>
<td>15 CTBN</td>
<td>1.64</td>
</tr>
<tr>
<td>20CTBN</td>
<td>1.71</td>
</tr>
<tr>
<td>25CTBN</td>
<td>2.77</td>
</tr>
</tbody>
</table>
3.3 Phase diagram

Phase diagram was constructed by assuming both oligomers as monodispersed and has computed the interaction parameters as a function of temperature from Flory-Huggins equation on free energy of mixing. Wang and Zupko [52] have observed an upper critical solution temperature (UCST) behavior while measuring the cloud point temperature of blends of epoxy monomers based on DGEBA and CTBN. They have reported a precipitation threshold located nearly at a CTBN volume fraction of about 0.07. Montarnal et al. [53] discussed the experimental aspects of cloud-point curves (CPC) of DGEBA-CTBN systems. Vazquez et al. [54] reported cloud-point temperatures as a function of CTBN content in DGEBA-amine system.

The measurement of the cloud-point temperature was based on the change in the intensity of the transmitted light at the time of phase separation. This is attributed to the change in the refractive index ($\mu$) of both phases. ($\mu = 1.57$ for epoxy and 1.51 for pure CTBN) [55]. Attenuation effect would appear for dispersed particles having an order of diameter greater than 100 nm. The shape of CPC depended on the polydispersity in the composition of CTBN random copolymer chains.

As cure reaction proceeds, network formation develops, epoxy becomes dense and refractive index comes closer to that of the elastomer resulting in the decrease of total scattered intensity. On the other hand, elastomer droplets become larger at the expense of smaller droplets as curing proceeds, and are become too large to contribute to the scattering in the experimental q-windows. This leads to the phase separation. Thus the very origin of the demixing of CTBN from the epoxy matrix is the increase in the average molecular weight of the thermoset during polymerization.

The mean-field Flory-Huggins model assumed that both components were in the monodispersed state with molar masses corresponding to the
number average of the corresponding distributions. It is believed that the
spinodal curve depended only on the weight average molecular weight and
the critical point depended on the weight average and z-average molecular
weights [56].

According to Gibbs equation, the free energy of mixing of component $A$ of
molar volume $V_A$ with component $B$ of molar volume $V_B$, expressed per
unit volume of the mixture was given by [57]:

\[
\Delta G_{M/cm^3} = RT \left[ (\Phi_A/V_A) \ln \Phi_A + (\Phi_B/V_B) \ln \Phi_B \right] + \Lambda \Phi_A \Phi_B \quad (3.7)
\]

$A$ and $B$ represent CTBN copolymer and epoxy monomer respectively.
$\Phi_A$ and $\Phi_B$ are the corresponding volume fractions. In the above
equation, the first term represents the combinatorial part of the free energy
of mixing while the second term denotes the residual free energy of mixing.
This equation represents the definition for the polymer-polymer interaction
parameter $\Lambda$, expressed in unit of energy per unit volume.

Interaction between both components is frequently represented by a
$\chi$ parameter. On neglecting the composition dependence, $\Lambda$ and $\chi$ are
related as:

\[
\chi = \Lambda V_r / RT \quad (3.8)
\]

Where $V_r$ is a reference volume and it is normally defined as the molar
volume of the smallest component (epoxy monomer). Since the objective
of the study is to compare the miscibility of different systems, a reference
volume can be avoided and the interaction can be represented on a unit
volume basis, by means of $\Lambda$. 

The location of the binodal curve was estimated by solving the equation (1) for a common tangent in the plot of \( \Delta G_m \) vs. \( \Phi_A \). The spinodal curve arises from \( \frac{\partial^2 \Delta G_m}{\partial \Phi_A^2} = 0 \).

The coordinates of the critical point common to both curves are given by:

\[
\Phi_A = \frac{V_B^*}{\left( V_A^* + V_B^* \right)} \quad \text{------------------------ (3.9)}
\]

\[
T_c = \frac{(2\Lambda_c/R)}{\left( V_A^* + V_B^* \frac{\Lambda_c}{\rho_B} \right)^2} \quad \text{------------------------ (3.10)}
\]

The mass fraction of CTBN was calculated from the volume fraction by:

\[
\Phi_m = \frac{\Phi A \rho_A}{(\Phi A \rho_A + \Phi B \rho_B)} \quad \text{------------------------ (3.11)}
\]

Where \( \rho_A \) and \( \rho_B \) denote the densities of CTBN copolymer and epoxy monomer respectively. Using equations (3.9) and (3.11), composition of the critical point was calculated and the critical temperature \( T_c \) was obtained from the experimental CPC. From the equation (3.10), where \( T_c \) is expressed in Kelvin, the critical value of the interaction parameter was obtained.

A straight line, as shown in Fig. 3.15 was obtained by plotting the values of \( \Lambda_c \) as a function of \( T_c \). A correlation exists between the interaction parameter and temperature as:

\[
\Lambda = \Lambda_0 + \Lambda_T T \quad \text{------------------------ (3.12)}
\]

This equation assumes that there is no dependence of \( \Lambda \) on composition.

The fairly small dependence observed for polystyrene-polybutadiene pair support this assumption [57]. The best linear fit of the curve give \( \Lambda_0 = 10.15 \) J cm\(^{-3}\) and \( \Lambda_T = -1.01 \times 10^{-2} \) J cm\(^{-3}\)K\(^{-1}\).


**Figure 3.15:** Interaction parameter per unit volume as a function of temperature for epoxy-CTBN system

The interaction parameter per unit volume obtained from Flory’s equation-of-state consists of terms that give change in energy density due to foreign segment contact and change in the free volume of mixing. The first term has negative temperature dependence since it is inversely proportional to the square of the specific volume [57]. Fig. 3.16 depicts the calculated binodal and spinodal curves for the system along with experimental CPC.
A and B represent binodal and spinodal curves and the region between the curve is the metastable region. The bi-continuous structures, which are stable at a particular condition appears in the metastable region. But, as temperature increases the conditions of the system is constantly changing. As a result, the shapes of interconnected structures shall also change, until the system reaches to the binodal region.

3.4 Conclusion
The miscibility aspects, phase separation phenomenon and the resultant phase morphology development of epoxy-CTBN blends during cure were investigated by means of techniques such as SALLS, OM, and SEM. Both dynamic and isothermal curing conditions (100 and 120°C) were applied in light scattering studies for all modified epoxies with elastomers in the range
of 5 to 25 phr weight content. High temperature curing induced phase separation. The dynamic light scattering studies were able to identify miscibility as well as cloud point temperatures. The intensity profile was used to calculate the correlation length at different temperatures of curing. The early stage of demixing process was explained by Cahn-Hilliard theory. The time for the onset of phase separation increased with the weight content of elastomer in the blend. A spinodal demixing mechanism was identified from the isothermal scattering profile and from the developed bi-continuous morphology. The size of phase separated CTBN particles was estimated which increased with increase in weight content of elastomer. A phase diagram has been computed using Flory-Huggins equation.
Morphology Analysis and Toughening Mechanisms

The structure-property relationship of the cured blends usually depends on the morphological features evolved during curing. The morphological characteristics of the phase separated elastomers have effects on the toughening mechanisms operating in modified samples. Hence it is significant to analyze the morphological developments. Different techniques were employed to analyze the development of morphology due to particle growth. Optical microscopy (OM) has been successfully employed during the SALLS measurements to monitor the particle growth and has been reported under the light scattering (LS) measurements in the early part of this chapter. Scanning electron microscopy (SEM) is an important practice and has been widely employed in this study to reveal the texture and morphology of the phase separated systems. Atomic force microscopy (AFM) is useful to investigate the sub particle inclusions in the phase separated elastomer domains.

3.5 Morphology of CTBN-modified epoxies

Scanning electron micrograph image of the cryogenically fractured surface of the neat epoxy sample showed (Fig. 3.17) smooth, glassy, and rivery fractured surfaces with ripples. The relative smoothness of the fractured surface, irrespective of the presence of some shears deformation lines, indicates that no significant plastic deformation had occurred. The morphological development during cure can be correlated with the impact behavior. The ripples are due to the brittle fracture of the network, which accounts for its poor impact strength, as there is no energy dissipation mechanism operating here. High degree of miscibility between DGEBA and the hardener was also evident from the initial transparency of the neat epoxy blend.
The fractured surface of all CTBN-modified epoxies exhibited two phase morphology with a rigid continuous epoxy phase and a dispersed rubbery phase of isolated spherical particles.

**Figure 3.17:** SEM image of neat epoxy resin

**Figure 3.18:** (a) [i, ii, iii and iv] SEM micrographs of CTBN-modified epoxies at $T_{\text{cure}} = 140^\circ\text{C}$ [(i) 5 phr (ii) 10 phr (iii) 15 phr (iv) 20 phr]
The micrographs of CTBN-epoxy samples were quantified with a view to distinguish the phase separated particles in samples cured at different temperatures. Fig. 3.18 (a) [i, ii, iii and iv] and Fig. 3.18 (b) [i, ii, iii and iv] represent the micrographs of the CTBN-modified epoxies (5-20 phr) cured at 140 and 150°C respectively.

During the early stages of cure, the soft elastomeric phase was separated from the hard epoxy matrix. However, the epoxy phase contains a certain amount of dissolved rubber phase which was proved from DMTA analysis [58] and is reported in chapter 4. As the concentration of CTBN was increased, the domain size increased. This followed a similar pattern to
other epoxy-rubber blends [59]. Initially, CTBN was miscible, at a slightly higher temperature, with epoxy resin and as the cure reaction proceeded the molecular weight of the system increased and attained a situation where CTBN got phase separated from the epoxy at the onset of gelation process - a reaction induced phase separated system. A single phased homogenous system, thus, transformed into a phase separated gel state and finally to the glassy vitrified state, near $T_{\text{cure}}$. The segregation of the precipitated elastomeric phase is prominent at higher concentrations of rubber phase and this was the reason for the comparatively large particle size in such liquid rubber-modified epoxies. The morphological results for the samples cured at 140 and 150°C have been quantified to find the number average ($D_n$), area average ($D_a$), volume average ($D_v$) and weight average ($D_w$) of domain sizes and to compute the polydispersity index. The results are tabulated in Table 3.2.

**Table 3.2:** Dispersed particle size and polydispersity of the modified epoxies cured at different temperatures

<table>
<thead>
<tr>
<th>Composition (CTBN wt %)</th>
<th>Curing temperature (°C)</th>
<th>140</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D_n$</td>
<td>$D_a$</td>
</tr>
<tr>
<td>5 phr</td>
<td>0.84</td>
<td>0.85</td>
<td>0.90</td>
</tr>
<tr>
<td>10 phr</td>
<td>0.86</td>
<td>0.88</td>
<td>0.93</td>
</tr>
<tr>
<td>15 phr</td>
<td>0.87</td>
<td>0.92</td>
<td>0.97</td>
</tr>
<tr>
<td>20 phr</td>
<td>0.91</td>
<td>0.99</td>
<td>1.05</td>
</tr>
</tbody>
</table>
The number, area, weight, and the volume averages of the dispersed domains decreased with increase in temperature. The CTBN elastomer has a high level of polar acrylonitrile units, thus acquiring a higher degree of cure before phase separation of rubber occurs. Accordingly, this resulted in the formation of smaller particles because at higher degrees of curing the viscosity of the epoxy phase is higher, which would reduce the easiness of CTBN diffusion and of particle coalescence. At high curing temperatures, the rate of epoxy cure reaction is high. The onset of gelation was attained at a lesser time (DSC and rheology measurements confirm this), which resulted in a lower degree of coalescence of particles, and ultimately in the phase separation of smaller particles. The increase in the viscosity of the system, the difference in the solubility parameters, and surface tension of the rubbery phase [60] during the cure process, all added to the formation of particles. On the other hand, as curing temperature ($T_{cure}$) decreased particle size increased. The volume average domain size increased with concentration of CTBN content at a particular temperature. The polydispersity index was found to be greater than one in all cases.

The increase in the domain size of the dispersed CTBN phase with increasing concentration of CTBN is associated with the reagglomeration or coalescence of the dispersed rubber particles. The phenomenon of coalescence was more important at higher concentration of dispersed CTBN phase. This is because of the delayed cure reaction, principally due to dilution and viscosity factors, which resulted in the segregation of small rubber particles leading to form bigger domains.

The extent of coalescence varies, depending on the viscosity and elasticity ratio of the components. The compatibility and interaction of the rubber with the epoxy matrix are determined by computing the volume fraction and interfacial area of the dispersed rubbery phase. The volume fraction was estimated using the equation (2.12), which shows the isotropic nature
of volume fraction. Hence, the values measured in the micrograph plane are the same as those measured in the real volume. The volume fraction is regarded as an effective value because it is measured in the plane of crack propagation. As rubber concentration increases volume fraction also increases. The data is presented in Table 3.3.

<table>
<thead>
<tr>
<th>CTBN concentration (weight %)</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 phr</td>
<td>0.0432</td>
</tr>
<tr>
<td>10 phr</td>
<td>0.1171</td>
</tr>
<tr>
<td>15 phr</td>
<td>0.1659</td>
</tr>
<tr>
<td>20 phr</td>
<td>0.2097</td>
</tr>
<tr>
<td>25 phr</td>
<td>0.2397</td>
</tr>
<tr>
<td>35 phr</td>
<td>0.3071</td>
</tr>
</tbody>
</table>

The interfacial area is given by \(3\Phi / r\), where \(\Phi\) = volume fraction of dispersed phase, and \(r\) = domain radius. Increase in interfacial area indicates more interaction of the rubber domains with the epoxy matrix. The variation of interfacial area per unit volume as a function of CTBN concentration is plotted in Fig. 3.19. The interfacial area increased first and then decreased when the CTBN concentration changed from 15 to 20 weight %. This may be associated with the high extent of coalescence in this composition.

The size of the domain was observed to range mostly from 0.5 to 1\(\mu\)m in diameter and also showed a slight bimodal distribution. The percentage distribution versus particle size for 15 and 20 weight % CTBN is shown in Fig. 3.20. When 15 phr rubber was added, the average size of domain was found to be in the range of 0.5-1\(\mu\)m, and 68% percentage of domain was less than or equal to 1\(\mu\)m.
Inter particle distance ($\delta$) was computed from the volume fraction ($\Phi$) of the dispersed phase which, in turn, was derived from the domain diameter ($D$) as per the equations (2.12) and (2.13) in chapter 2. The values are furnished in Fig. 3.21.

![Figure 3.19: Interfacial area per unit volume and weight % of CTBN](image1)

![Figure 3.20: Percentage distribution versus domain size in epoxy-CTBN blend systems](image2)
The values showed a decreasing trend with the inclusion of higher weight % of elastomer. As the concentration of elastomer phase increased more rubber phase got phase separated and thereby the domain size increased. This caused a decrease in the inter particle diameter.

### 3.5.1 Co-continuous morphology development

In CTBN-modified epoxies, a tendency of shift in the morphology from dispersed to a continuous nature was noted from 25 phr elastomer modified epoxies. Typical SEM images of 25 and 30 phr epoxy-CTBN blends are demonstrated in Fig. 3.22 (i and ii). It is important to note that the rubber is not fully continuous in nature in these images. Both dispersed and continuous rubber particles are observed. Of course, continuous rubber phase morphology is expected in higher concentration of rubber-modified epoxies and was reported in an earlier publication [61]. Since, SEM is not a trustworthy method to distinguish between particulate and co-continuous morphology, a quantitative methodology based on extraction
has been performed to identify the morphology. The method is based on the extraction of the rubber phase from the epoxy-rubber blends.

![Figure 3.22: SEM micrographs of 25 and 30 phr CTBN- modified epoxy samples](image)

The results of the extraction in toluene for 24 hrs are furnished in Table 3.4. The percentage of extracted elastomer phase was found to be increased with rubber content. This is a signature of co-continuous tendency.

**Table 3.4: Results of the extraction of CTBN-modified epoxies**

<table>
<thead>
<tr>
<th>Weight % of rubber in the sample/sample code</th>
<th>Percentage of extracted rubber phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 CTBN</td>
<td>8.0</td>
</tr>
<tr>
<td>10 CTBN</td>
<td>11.0</td>
</tr>
<tr>
<td>15 CTBN</td>
<td>25.0</td>
</tr>
<tr>
<td>20 CTBN</td>
<td>33.0</td>
</tr>
<tr>
<td>25 CTBN</td>
<td>45.0</td>
</tr>
<tr>
<td>30 CTBN</td>
<td>53.0</td>
</tr>
</tbody>
</table>
A schematic representation of the development of co-continuous morphology on the addition of higher weight % of elastomer is depicted in Scheme 3.1.

Scheme 3.1: Schematic representation of co-continuous morphology in CTBN-modified systems. A and B are blend systems having lower and higher weight % of CTBN.

In a cured blend of epoxy/liquid rubber, having a lower concentration of elastomeric particles, the phase separated domains are dispersed in the matrix, and this state is represented by the Scheme 3.1(A). The particles are well dispersed and separated with each other. However, the phase-separated domain distribution in a cured blend with the incorporation of higher weight % of elastomer is different. At higher concentration of rubber, generally, there will be an increase in size and number of particles. The phases separated particles come closer during cure and show a tendency to form co-continuous morphology 3.1(B).

3.5.2 Toughness characteristics of CTBN-modified epoxies

The morphology generated during cure is greatly responsible for the toughness characteristics of modified epoxies. When a CTBN concentration of 15 weight % was added, the average domain size, as already noted, was found to be in the range of 0.5-1.0 µm. Several studies [61-62] have suggested that particle size influences the extent and type of toughening micro mechanism, and so affect the measured toughness. According to the
proposal of Sultan and McGarry [62], large particles (0.5-1 µm) are five times more effective in toughening the thermoset than small particles of size around 0.01 µm. Thus a critical particle size of 0.5-1 µm can cause sufficient stress transfer in the matrix.

The impact behavior of the cured epoxy can be explained based on the two-phase nature of the system. According to Beaumont and co-workers [63], the rubber particles are considered to bridge the crack as it propagates through the material. Thus the rubber particles are able to prevent the crack growing to a catastrophic size. Bridging of cracks is represented in the SEM micrograph in Fig. 3.23. The increase in toughness is due to the amount of elastic energy stored in the rubber particles during stretching. Thus, the deformation of the rubber particles in the matrix is responsible for sufficient stress transfer and hence impact enhancement.

Shear yielding of the matrix is another reasonable mechanism that may be operating. According to Newman and Strella [64], the principal function of the rubber particle is to produce sufficient triaxial tension in the matrix so as to increase the local free volume and hence enable extensive shear yielding of the matrix. Thus crack bridging of rubber particles along with shear yielding is the main toughening mechanism and is responsible for the enhancement of impact behavior.
Morphological examination using microscopic techniques further revealed some insight into the toughening mechanism operating in CTBN-modified epoxies. A comparison of morphology of the fractured surface of a 10 phr elastomer–modified sample prepared under two different methods revealed some interesting aspects on toughness characteristics. One of the SEM samples was prepared by simple fracture after putting in liquid $N_2$ for some time. The fractured surface was extracted in solvent for etching out the elastomeric phase before microscopic analysis. The SEM of the fractured surface of the sample is presented in Fig. 3.24 (a). Another sample of the same composition was prepared from a similar formulation, which was subjected to crack initiation by applying stress using a double cantilever mode. After extraction in the solvent, a small block in the vicinity of the crack was cut off in liquid $N_2$. Representative micrographs of the fractured surface near the crack tip are depicted in Fig. 3.24 (b).
Figure 3.24 (a) and (b): SEM images of fractured surfaces of 10 phr CTBN-modified epoxies. (a) Simple fracture and extraction (b) Crack initiation by stress followed by extraction.

Fig. 3.24 (a) showed dispersed spherical domains with an average particle diameter of (0.72 µm). On the other hand, Fig. 3.24 (b) which represented elastomeric domains near the crack tip were almost elliptically deformed with a noteworthy difference in the average particle diameter of (1.4 µm). This showed the development of some sort of cavitations of the rubbery phase near the crack tip during loading. The nature of the elastomeric phase showed that deformation has occurred along the direction of the applied stress. From the nature of these SEM micrographs, we could arrive at the conclusion that the mechanism of toughening in CTBN-modified epoxies is also attributed to cavitations of elastomeric particles, which is followed by shear deformation of the epoxy matrix. This observation is fully in agreement with the theory of Yee [65-66] who reported cavitations of rubber particles and shear deformation of epoxy matrix as the chief mechanisms in elastomer-modified epoxies. The increase in impact strength and fracture toughness could be due to the increase in stress transfer. The stress transfer from epoxy matrix to elastomeric domains with
increase in total surface area of particles could be explained as the reason for the total toughness of the modified epoxy.

3.5.3 Phase inversion in CTBN-modified epoxies

During the mechanical analysis it was observed that as the volume fraction of dispersed rubbery phase increased, toughness also increased. But the modulus and yield stress decreased slightly. At first, the fracture energy, $G_{IC}$, increased with respect to the volume fraction. But after attaining a maximum of 15 weight % it decreased slightly. This may be due to the flexibilization of the epoxy matrix by dissolution of rubber. Higher concentrations of CTBN, for e.g. from more than 30 weight % of elastomer content, will lead to plasticization effect. Interfacial area was found to have higher values, to a certain extent, for larger percentage distribution of CTBN. At higher concentration, a reversal of morphological characteristics occurs, resulting in the embedding of epoxy particles in elastomeric matrix. This transitionary behavior is accounted by a process known as phase inversion (Fig. 3.25). The morphology as well as the mechanical characteristics underlines this. Also, this was proved from extraction studies. Within this regime, the mode of failure was found to be dramatically different from that observed with the elastomer particle dispersions. The high CTBN concentration systems exhibited rubber-like behavior.
3.5.4 Theoretical study on co-continuity morphology

The theoretical value of $(\% R)_{crit}$ may be obtained by applying the Flory Huggins equation. It is assumed that CTBN is a mono dispersed compound with a molecular weight equal to the number average molecular weight. Also, the epoxy-anhydride solvent is assumed to be a pure compound with a number average molecular weight equal to that of the neat system at the conversion of phase separation [67]. Again, it is to be assumed that there is no reaction between the rubber and the epoxy-anhydride copolymer.

The volume fraction of rubber at the critical concentration for co-continuity is given by [68]

$$\Phi_R = \frac{1}{1 + \left(\frac{V_{CTBN}}{V_{E-A}}\right)^{1/2}}$$  \hspace{1cm} (3.13)

where $V_{CTBN}$ and $V_{E-A}$ are the molar volumes of CTBN and thermoset, respectively, at the conversion point of phase separation (both are taken as pure compounds). The elastomer, CTBN used in this study has a number
average molecular weight, $\bar{M}_n = 3500$ g / mol, and a density of 0.9045 g / cm$^3$. Its molar volume is $V_{CTBN} = 3869.5$ cm$^3$ / mol.

The initial molar volume of the stoichiometric thermoset may be defined by [67]

$$V_{E-A}^0 = \frac{(M_A + 2M_E)}{3\rho_{E-A}} \quad \text{(3.14)}$$

where $M_A$, the anhydride molecular weight is 162 g/mol, $M_E$, the epoxide molecular weight is 348 g/mol, and the density of the neat thermoset, $\rho_{E-A} = 1.125$ gm / cm$^3$.

We get $V_{E-A}^0 = 254.22$ cm$^3$ / mol.

However, for a $A_4 + E_2$ polymerization, the increase in molar volume with conversion is given by [67]

$$V_{E-A} = V_{E-A}^0 / \left(1 - 4x/3\right) \quad \text{(3.15)}$$

where $x$ is the conversion at the cloud point for the range close to the critical concentration. The value is calculated as $x \approx 0.1$ in an epoxy system. Then $V_{E-A} = 293.2$ cm$^3$ / mol and the volume fraction of rubber at the critical concentration for co-continuity is $\Phi_R = 0.215$. From the morphology studies, the above value of volume fraction of rubber at the critical point appears when the CTBN concentration is in the range of 20-25 weight percentages (refer Table 3.3).

Addition of CTBN to the epoxy reduces the $T_g$ value of cured neat epoxy to a certain extent. It appears that most of the CTBN had formed phase-separated rubber phases rather than remaining unreacted in the epoxy-rich phase as a plasticizer. The reduction in $T_g$ values due to rubber inclusion (in fact, the reduction was more prominent at higher elastomer concentrations) means that the excess elastomer remained in the epoxy had flexibilized the matrix. On the other hand, the $T_g$ of the CTBN phase was found to be slightly
enhanced as the concentration increases. This is probably due to the inclusion of some part of epoxy into the CTBN domains. (The data of $T_g$ is included in chapter 5 under DMTA explanations).

3.5.5 AFM analysis of epoxy-CTBN blends

Atomic force microscopy (AFM) images were employed to view the sub inclusion of epoxy particles in the phase separated elastomer domains. Typical AFM images of CTBN-modified epoxies obtained by two different instrumentations are illustrated below. Fig. 3.26 depict different views of the topographic [(a) and (b)] and phase images [(c) and (d)] of epoxy-CTBN (10 phr) blend system. The elastomer domains can be viewed clearly in (c) and (d).
Figure 3.26: (a), (b), (c) and (d) AFM images of epoxy-CTBN (10 phr) blend

Another view on the AFM images of 10 phr CTBN-epoxy blend are illustrated in Fig. 3.27 (a), (b) and (c). The AFM probe is demonstrated in (a) whereas topographic and phase images are represented in (b) [i and ii] respectively.
Figure 3.27: (a) and (b) [i] topographic and [ii] phase image views of epoxy-CTBN (10 phr) blend.

Fig. 3.27 (c) depicts the 3D representation of the topographic image. The x, y and z axis are 60.0, 60.0 and 1.1 µm respectively.

Figure 3.27: (c) 3D view of epoxy-CTBN (10 phr) blend
Fig. 3.28 (a), (b) and (c) represents the AFM images of 15 phr CTBN-epoxy blend system. The AFM probe [Fig. 3.28 (a)] together with topographic and phase images (Fig. 3.28 (b) [i and ii]) are demonstrated.

**Figure 3.28: (a)** 15 phr CTBN-epoxy blend system

(i) **Figure 3.28: (b)** [i] topographic and [ii] phase images of epoxy-CTBN (15 phr) system

The 3D representation of the topographic image of the sample is depicted in Fig. 3.28 (c). The x, y and z axis are 80.0, 80.0 and 1.4 µm respectively.
The topographic [(a) and (b)] and phase images [(c) and (d)] of 25 phr CTBN-epoxy blend system are depicted in Fig. 3.29. Sub inclusions in the elastomer domains can be viewed clearly in (c) and (d).
Figure 3.29: (a)-(d) AFM images of epoxy-CTBN (25 phr) system

Morphology of HTPB-modified epoxies

3.6 Morphology and toughening behavior

The cryogenically fractured surfaces of blends, Fig. 3.30 [i, ii, iii and iv], represent 5 to 20 phr HTPB-modified epoxies which clearly show two distinct phases- a continuous epoxy matrix and dispersed rubber phase. The samples were opaque due to heterogeneous morphology. The holes developed in the SEM micrographs were due to the extracted particles from the surface of the samples after treatment with toluene for 12 hrs. The domain parameters of the phase separated blends were quantified [69] and the results are furnished in Table 3.5.
Figure 3.30: [i, ii, iii and iv] SEM micrographs of epoxy-HPB (5-20 phr) blends [(i) 5 phr (ii) 10 phr (iii) 15 phr (iv) 20 phr]

Table 3.5: Morphological parameters of dispersed HTPB domains in the epoxy matrix

<table>
<thead>
<tr>
<th>HTPB content (phr)</th>
<th>$\bar{D}_n$</th>
<th>$\bar{D}_a$</th>
<th>$\bar{D}_w$</th>
<th>$\bar{D}_v$</th>
<th>$D_n/D_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.82</td>
<td>0.85</td>
<td>0.91</td>
<td>1.46</td>
<td>1.10</td>
</tr>
<tr>
<td>10</td>
<td>0.90</td>
<td>0.96</td>
<td>1.07</td>
<td>1.52</td>
<td>1.18</td>
</tr>
<tr>
<td>15</td>
<td>1.2</td>
<td>1.4</td>
<td>1.7</td>
<td>2.3</td>
<td>1.41</td>
</tr>
<tr>
<td>20</td>
<td>1.5</td>
<td>1.8</td>
<td>2.2</td>
<td>2.8</td>
<td>1.52</td>
</tr>
</tbody>
</table>

The size of the precipitated rubbery domains increased with increase in elastomer content of the formulations. Number and area average domain
diameters were found to increase with respect to rubber content, which is in agreement with the behavior of other rubber-modified epoxies. The increase in domain size with the incorporation of rubber is attributed to the coalescence of the dispersed rubber particles, which depends on viscosity and elasticity ratio. This becomes more prominent in higher weight content of the dispersed rubber phase.

In epoxy blends having 5 and 10 weight % of rubber, depicted in Fig. 3.30 [i and ii], the particles were uniformly distributed throughout the matrix with a narrow particle size distribution. This kind of unimodal distribution of small particles was responsible for lower crack growth in these specimens which was indicated by the presence of relatively large number of deformation lines. Also, the fracture surfaces, unlike neat epoxy, were not very smooth, indicative of a ductile manner of fracture.

According to Yee and Pearson [70] the size of stress whitened zone or the amount of deformation lines are proportional to the increase in toughness of the material. Relatively distorted shape of rubber domains in these cured resin matrices is supposed to be ascribed to the higher amount of plastic deformation. The deformation lines were propagated through rubber domains, promoting stress transfer between the particles and epoxy matrix. Also, less brightness of the interfacial layer around the rubber domains in lower modified epoxies compared to higher modified samples are indicative of the interaction between the particles and epoxy matrix [71].

In order to operate the yielding process throughout the matrix, a homogenous distribution of smaller particles is necessary. This morphological structure is believed to be responsible for the highest impact performance of modified epoxies. Thus uniformly distributed rubber particles act as stress concentrators and exhibit highest impact strength than unmodified epoxy.
Rubber-modified samples containing 15 and 20 phr HTPB, represented by [iii and iv] of Fig. 3.30, were characterized by a heterogeneous particle size distribution. A wide range of particle size distribution was observed in these samples. The particle size distribution in a blend containing 20 phr HTPB is illustrated in Fig. 3.31.

![Figure 3.31: Particle size distribution in 20 phr rubber-epoxy blend](image)

The particle size distribution has a wide range from 0.1 to 60 µm. A number of particles were situated in the range of 15-28 µm. The frequency of percentage of higher particle size was predominant in modified epoxies containing higher weight content of the elastomer. The heterogeneous morphology developed in high concentrated blends can be correlated with gelation time. The gelation time increases as the concentration of the rubber increases due to viscosity and reduced reactivity factors. During the polymerization reaction, small particles agglomerated and increased in size to form bigger particles. Thus there was enormous chance for coalescence of particles having varying size distribution. The poor mechanical performance
of high rubber filled systems shall also be attributed to this heterogeneous nature of particle size distribution.

Interfacial area per unit volume in HTPB-epoxy blends are represented in Fig. 3.32. The value increased up to 10 phr rubber concentration and then showed a decreasing trend. The lower values of interfacial area compared to CTBN-epoxy systems showed that the interaction of HTPB rubber with the epoxy matrix was poor. When the HTPB content was more, the phase separated elastomer domains were bigger due to the tendency of agglomeration of particles. This further reduced the interaction with the matrix and as a result the values were low.

![Graph showing interfacial area per unit volume as a function of weight content of HTPB](image)

**Figure 3.32:** Interfacial area per unit volume as a function of the weight % of HTPB

Fig. 3.33 represents the inter particle distance in HTPB-epoxy systems estimated as per the expressions (2.13) and (2.14) in chapter 2.
The value decreases with the introduction of more elastomer content. Since the elastomer is not miscible in the resin the phase separated domains are big as compared to the domains of CTBN elastomer. Hence the inter particle distance due to elastomer particles in epoxy-HTPB blend system is shorter than in CTBN-epoxy system having the same composition of elastomer. Also, the inclusion of still more weight % of elastomer generates bigger domains probably due to the agglomeration of particles, and thus the distance between the particles further reduces. CTBN-epoxy system also shows similar observation.

The mechanical performance of HTPB-modified epoxies, discussed in chapter 6, revealed that the addition of rubber imparts an increase in the value of $K_{ic}$ and $G_{ic}$ up to an optimum rubber content of 10 phr only. Further increase was not observed on additional loading of rubber. Agglomeration of rubber particles at higher concentrations is supposed to be the reason for this.
The improvement in toughness, as explained by Kinloch and Hunston [72], is ascribed to the rubber particles that enhance shear localization by acting as stress concentrators. Hydrostatic tension ahead of the crack tip causes rapid cavitations of the rubber. The voided damage zone then blunts the crack, which behaves as if it had a much larger crack tip radius. Thus a larger plastic zone gets associated with this crack and this is the source of toughening effect. The rubber particles that are bonded to the matrix can bear the load in triaxial tension. Thus, interfacial interactions of rubber particles with the matrix epoxy is desirable for toughness property which can be assigned to the pre-reaction of the rubber thereby improving toughness by increasing the miscibility of rubber into the epoxy matrix. Hence some amount of rubber goes into the epoxy matrix and act as plasticizer. If the rubber is incorporated into the epoxy network, it acts as a flexibilizer. Both of these effects increase the ability of the matrix to deform under shear. But, since HTPB has no appreciable miscibility with the resin, plasticization of the matrix is practically zero and only flexibilizing effect operates. This is, perhaps, the reason for the slow increase of $K_{IC}$ values with rubber loading. Reduction in cross-link density may also add to this. The curing followed by the phase separation of the elastomer phase is schematically represented in Scheme 3.2. The Scheme represents the conversion of a homogeneous system to a phase separated three dimensional system.

The double headed and single arrows in B symbolize the bonding of elastomer-hardener-epoxy and epoxy-hardener respectively. In C the double headed and single arrows correspond to three-dimensional base matrix of epoxy network and phase separated domains of neat HTPB respectively. The polymerization starts mainly with the reaction between hardener and epoxy, represented by the bond formation between them. During the cure reaction few of the elastomers react with the hardener,
Scheme 3.2: Schematic representation of phase separation behavior in HTPB-modified epoxies. A: Individual components initially present in the system such as epoxy, hardener, and rubber units which are represented by square, circle and short arrow respectively. B: Different possibilities of bonding during curing. C: Phase separated system.

forming elastomer-hardener-epoxy network. Most of the HTPB units remain as such without involving in the cure reaction. Figure B represents this state of curing. Meanwhile, as the molecular weight of the system increases, rubber gets phase separated to form domains, which are almost pure HTPB. This state is depicted by C in the Scheme.

3.7 Co-continuous morphology development

Unlike CTBN, the hydroxyl- terminated liquid rubber, HTPB, was initially immiscible in the resin. Therefore the phase separated HTPB particles were bigger in size in comparison to that of the phase separated CTBN domains, at a constant elastomer concentration. The inclusions of a higher weight % of elastomer, surely led to the agglomeration of smaller particles. Since HTPB was almost insoluble in the epoxy resin, co-continuous nature
of morphology was evolved by a lesser amount of rubber inclusion as compared to CTBN elastomer. When the rubber content was above 20 phr the rubber particles were close to one another and noticed a tendency of formation of continuous phase. Since the elastomer was insoluble in epoxy, it seemed difficult to get good samples of modified epoxies having HTPB greater than 20 weight %. As in the case of CTBN samples, quantitative method based on extraction was employed for the investigation of co-continuous nature of morphology since SEM images showed particulate morphology. The result of the extraction is furnished in Table 3.6. The increase in the extracted elastomer phase with the inclusion of more rubber component is a signature of the co-continuous morphology. In comparison to CTBN-modified epoxy blends, the percentage of extracted elastomer phase was more in these systems. This was due to the poor miscibility of HTPB in epoxy resin which resulted in poor interaction.

### Table 3.6: Results of extraction of rubber-modified epoxies

<table>
<thead>
<tr>
<th>Weight % of elastomer in the sample/sample code</th>
<th>Percentage of extracted HTPB phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 HTPB</td>
<td>12.0</td>
</tr>
<tr>
<td>10 HTPB</td>
<td>25.0</td>
</tr>
<tr>
<td>15 HTPB</td>
<td>40.0</td>
</tr>
<tr>
<td>20 HTPB</td>
<td>68.0</td>
</tr>
</tbody>
</table>

3.8 AFM analysis of epoxy-HTPB blends

Topographic and phase measurements have been done in 5 phr HTPB-epoxy blends to view the phase separated elastomer in the blend which are depicted in Fig. 3.34 (a), (b) [i and ii] and (c). (a) represents a topographic image.
In the 3D representation of the topographic image of the system, the x, y and z axis are 60.0, 60.0 µm and 595.5 nm respectively.

Figure 3.34: (a), (b) and (c) AFM micrographs of epoxy-HTPB (5 phr) blend
3.9 Conclusion

The ultimate morphology of epoxy-CTBN/HTPB blends during cure differed in terms of the morphological parameters of phase separated elastomer domains. The phase separated rubber domains were bigger in epoxy-HTPB systems than in epoxy-CTBN systems having the same amount of rubber. This was due to the difference in the miscibility aspects of the elastomers in epoxy resin during curing. CTBN was miscible in the resin during curing which resulted in better interfacial adhesion with the resin matrix. On the other hand, the poor miscibility behavior of HTPB in the resin generated reduced interaction with the epoxy matrix. Different toughening mechanisms prevailing in elastomer-toughened epoxies were discussed. Plastic deformation and shear yielding of the matrix as well as crack bridging are the major mechanisms operating in CTBN-toughened epoxies. Cavitation due to the rubber phase has also some role in toughening aspects. Inclusion of higher weight % of elastomers caused phase inversion. Based on Flory Huggins equation, the percentage of CTBN at the critical composition has been explained. The inter particle distance in HTPB-modified epoxies were higher compared to CTBN-modified matrices. Development of shear localization by rubber particles was explained as the major toughening mechanism prevailing in epoxy-HTPB matrices. Reduction in cross-linking density due to the occupancy of the elastomer in the epoxy matrix also contributed to the toughness characteristics of the matrix. A combined effect of all these properties caused improved mechanical properties more in CTBN-systems than in HTPB-epoxy blends. Finally, the morphology was analyzed using AFM technique.
References


