Chapter 8

Mechanical Performance and Nanoindentation Analysis of CTBN/HTPB-Modified Epoxies

The function of the modification of epoxy resin with liquid rubbers is to achieve toughened epoxy polymeric materials having better ultimate properties. The chapter deals with various bulk mechanical properties of rubber-modified epoxies and a critical comparative account of the properties based on the difference in miscibility and morphology of the cured network. Also discusses the localized mechanical properties by nanoindentation analysis. Mechanical properties include tensile properties and toughness characteristics. The principle parameters that quantify the toughness properties such as fracture toughness and fracture energy were quantified. Impact strength measurements were also done on modified blends. Flexural property, heat deflection temperature and hardness of modified blends were also computed from standard tests. The change in the trend of various properties with respect to the elastomer content was also discussed. Nanoindentation technique provided an opportunity to quantify modulus and hardness of the elastomer-modified epoxies. Finally, an attempt has been made to correlate impact properties with the ratio of modulus to hardness obtained from nanoindentation studies.

Parts of the results of this chapter
i. have been communicated to Chemistry of Materials
he dispersed rubber particles can greatly improve the globalized mechanical properties of the epoxy matrix, which are studied by the use of conventional bulk material testing techniques, for instance, tensile test is used to characterize elastic modulus of rubber-modified epoxies. It is to be noted that in rubber-modified thermoset resins micro-voids are generated. In fact, cracks are initiated from micro-voids or debonding positions and extended to other micro-voids and ultimately lead to catastrophic failure of the matrix. It has been widely accepted that dispersed rubber particles in the epoxy matrix prevent crack propagation by acting as crack terminators and this has been suggested as a prominent mechanism of toughening [1-3].

Since the ultimate aim of toughening epoxy matrix is to attain best mechanical performances, for e.g., improvement in impact strength and fracture toughness, the characterization and quantification of mechanical properties are significant.

In a work done by Tripathi and Srivastava [4], butadiene acrylonitrile rubber was proved to improve the impact property of epoxy resin. Dean et al. [5] have manufactured multiscale fiber-reinforced nanocomposites using a vacuum assisted resin infusion molding (VARIM) process. An improvement of 31% in flexural modulus and 24% in flexural ultimate strength for the 2% silicate fiber-reinforced nanocomposites was achieved. Interlaminar shear and fracture toughness studies were also conducted.

But at the microscopic point of view, the existence of micro-voids will enhance the failure of the matrix, as they are crack initiators. This underlines the scope of the study of the localized mechanical properties of rubber-incorporated epoxies, as it is an important factor for understanding the integrity, internal properties, and uniformity of the blend matrix. Investigations on the localized mechanical behaviors of rubber-epoxy
blends are significant for manufacturing an infrastructure that minimizes the risk of void formation.

Nanoindentation is an efficient technique recently invented by Oliver and Pharr [6] and is effective to determine the localized material properties. It provides facility to the nanoscopic measurements of elastic modulus, micro-hardness, and contact stiffness of a material [7-8]. In the last few decades numerous researchers have employed this technique to explain mechanical properties of rigid particulate filled polymeric materials [9-10]. In a recent study, reported by Woo et al. [11], the residual mechanical properties of epoxy-organoclay nanocomposites after moisture and UV exposure have been evaluated. The microhardness and the modulus of the surface material were determined from nanoindentation and found to be increased after UV exposure. Recently, phosphated epoxy acrylate and phosphated imide-epoxy were synthesized [12] and used as compositions of non-volatile (no solvent) UV curable ink for manufacturing the jet-printed LCD color filter (CF). nanoindentation technique was used to measure the hardness and the modulus of the printed blue stripes.

In a recent study, Nanoindentation technique analysis was employed [13] to find the nanohardnesses of the various phases (the fiber, the interface and the matrix) in the armos fibers/epoxy resin composites. Li et al [14] have employed nanoindentation tests to characterize the mechanical properties of coiled nanotubes in epoxy matrix. Lam and Lau [15], have reported on the investigation of the enhancement of mechanical properties by the use of nanoclay platelets in epoxy resin. They have employed nanoindentation technique to find the elastic modulus of nanoclay/epoxy composite samples made under different sonication temperatures and compared their localized mechanical behaviors. In a particular study, nanoindentation technique has been employed [16] to find the transverse elastic modulus of PAN-based carbon fibers. Thus nanoindentation
analysis is widely employed to characterize mechanical properties of blends and composites in the nano scale range.

8.1: Mechanical properties of elastomer-modified epoxies
Epoxy-CTBN systems

8.1.1 Tensile properties
The influence of stress-strain curves for the cured resins with different weight % of CTBN content is shown in Fig. 8.1 and the mechanical properties of the cured systems with various loadings of CTBN are furnished in Table 8.1. The brittle fracture of neat epoxy and the ductile failure mode of modified samples were evident from the curves. The ductile behavior is attributed to better energy dissipation mechanism of the dispersed rubber particles in the epoxy matrix. The results of the mechanical properties indicate that the cured resin having CTBN content in the range of 10 to 15 phr showed the best of balance of properties. The decrease in the tensile strength and tensile modulus were due to the presence of some amount of dissolved rubber in epoxy which increased with the inclusion of more weight percentage of rubber. The young’s modulus decreased with the inclusion of low modulus rubber content. The relative amount of dissolved and phase-separated rubber increased when the initial rubber content increased. The area under the stress-strain curve which is a measure of toughness was moderately higher for the modified epoxies having CTBN concentration in the range of 10-15 weight %.
Figure 8.1: Stress-strain curves of epoxy-CTBN systems

Table 8.1: Tensile properties at room temperature with different loadings of CTBN

<table>
<thead>
<tr>
<th>CTBN (phr)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Percentage elongation</th>
<th>Toughness(^a) (× 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80</td>
<td>1913</td>
<td>4.70</td>
<td>2.10</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>1457</td>
<td>6.00</td>
<td>2.30</td>
</tr>
<tr>
<td>10</td>
<td>71</td>
<td>1328</td>
<td>6.10</td>
<td>2.70</td>
</tr>
<tr>
<td>15</td>
<td>69</td>
<td>1245</td>
<td>6.60</td>
<td>2.80</td>
</tr>
<tr>
<td>20</td>
<td>63</td>
<td>1099</td>
<td>6.70</td>
<td>2.81</td>
</tr>
<tr>
<td>25</td>
<td>50</td>
<td>906</td>
<td>7.10</td>
<td>2.81</td>
</tr>
</tbody>
</table>

\(^a\)Area under the stress-strain curves expressed in Joules
Epoxy-HTPB systems
Stress-strain behaviors of the HTPB-modified epoxies are shown in Fig. 8.2. The Figure clearly showed that the curve for 10 phr HTPB blend occupies a larger area than other higher modified ones. The neat epoxy underwent brittle fracture due to its rigid nature. The high rubber filled epoxies also showed a tendency towards brittle nature of failure as read from the curves. The energy transfer mechanism operating in HTPB phase separated epoxy matrix will not be sufficient to set aside the matrix from failure to an extent equivalent to CTBN-epoxy matrix. However, it was subjected to a certain elongation before failure which was indicated by the decline in the rigidity of the epoxy matrix. The poor performance in the % of elongation as compared to CTBN systems may be due to its immiscible nature in epoxy which resulted in poor interaction with the matrix. The various tensile properties for different loadings of the rubber are formulated in Table 8.2. Low modulus elastomer reduced the tensile strength of neat epoxy system. But, the reduction due to HTPB was less than due to CTBN having equivalent weight content. This again points to the low level of interaction of HTPB with the epoxy matrix.

![Stress-strain curves of epoxy-HTPB blends](image)

**Figure 8.2:** Stress-strain curves of epoxy-HTPB blends
Table 8.2: Tensile properties at room temperature with different loadings of HTPB

<table>
<thead>
<tr>
<th>HTPB weight % (phr)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Percentage elongation</th>
<th>Toughness&lt;sup&gt;a&lt;/sup&gt; (× 10&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80</td>
<td>1913</td>
<td>4.70</td>
<td>2.10</td>
</tr>
<tr>
<td>5</td>
<td>76</td>
<td>1814</td>
<td>4.90</td>
<td>2.15</td>
</tr>
<tr>
<td>10</td>
<td>73</td>
<td>1765</td>
<td>5.00</td>
<td>2.20</td>
</tr>
<tr>
<td>15</td>
<td>69</td>
<td>1730</td>
<td>5.10</td>
<td>1.80</td>
</tr>
<tr>
<td>20</td>
<td>65</td>
<td>1700</td>
<td>5.10</td>
<td>1.60</td>
</tr>
</tbody>
</table>

<sup>a</sup>Area under the stress-strain curves expressed in Joules

When HTPB gets incorporated into the thermoset matrix, its elastomeric character authorizes a comparatively small decrease in tensile strength and young’s modulus as well as a small increase in elongation as compared to the CTBN which led to significant change in tensile properties. For instance, the inclusion of 10 and 15 weight % of CTBN recorded a reduction of 11 % and 15 % in tensile strength, whereas the corresponding decline in HTPB addition was only 8 and 13 %. Similarly, the change in the young’s modulus was 30 % and 35 % when the CTBN inclusion was 10 and 15 weight content (phr) respectively. For HTPB-epoxy system it was only about 8 % and 10 %. This illustrated the lack of interaction, via solubility and reaction, between epoxy and HTPB elastomer. The slight reduction in the properties may be rationalized by the lowering in cross-linking density of the epoxy-rubber network as the modifier occupies the reaction centers during modification. Since the decrease in tensile strength with rubber content can be related to the stiffness of the modified network, the decrease in stiffness of the network...
epoxy shall be due to the lowering in cross-link density on rubber addition. Since HTPB is less compatible with the resin, the volume fraction of the dispersed rubber phase becomes more significant which reduces the interaction with the epoxy matrix. The volume fraction increases with the increase in the addition of the elastomer.

8.1.2 Impact and flexural properties

Epoxy-CTBN systems

The impact strengths of elastomer-incorporated epoxy blends are depicted in Fig. 8.3. The CTBN-epoxy blends having 10-15 phr elastomer content exhibited greater impact strength which means that the systems are likely to absorb greater impact energies. Maximum impact strength was observed in 15 phr elastomer-modified system. Modified epoxies having 10 and 20 phr CTBN showed 4.5 and 22.5 % decrease from the maximum value.

![Figure 8.3: Impact strength of CTBN-modified epoxies](image)

The impact properties are closely associated with the morphological development of the cured network. When the CTBN concentration was in
the range of 10-15 weight %, the average domain size, as already mentioned, was found to be in between 0.5-1.0 µm. As per the established mechanism, optimum impact properties are attained with rubber particles having sizes in the range of 0.5-1.0 µm or so. Crack bridging of rubber particles and shear yielding of the matrix are also responsible for improved impact properties. The effects of these mechanisms in improving the impact properties and overall toughness behavior of the matrix were discussed in chapter 3.

In modified epoxies having higher weight content of CTBN, the matrix may get flexibilized by the elastomer, rather than toughened, since it is soluble in epoxy. The phase separated elastomer domains were bigger as recognized from the morphology, where the stress-transfer mechanism is feeble. This deteriorated the impact strength. However, the matrix ductility due to the presence of elastomer was the source of the better impact strength as compared to the neat matrix.

Fig.8.4 demonstrates flexural properties of CTBN-epoxy blends. The flexural properties of the modified resins decreased with increase in rubber concentration, compared with those of the parent epoxy resin. This is due to the incorporation of the low modulus elastomer component.
Epoxy-HTPB systems

The results of impact strength of resin samples containing different amounts of HTPB are depicted in Fig. 8.5. All modified networks showed higher impact resistance than neat resin. However, the property attained a maximum for 10 phr rubber content and above this optimum level of rubber content, a falling tendency was noted. The increase in value up to an optimum level of rubber concentration was attributed to the effective stress concentration and stress transfer behavior of phase separated rubber-rich particles that amplify plastic deformation of a highly brittle matrix to a certain extent. The blend network containing 10 phr rubber has a maximum impact strength value of 0.258 J which was about 45 % higher than that of neat epoxy while for 20 phr rubber the value was 30 % lower than the maximum. However, 20 weight % blend exhibit a better performance than the neat one. Comparatively lower performance of HTPB than CTBN may be attributed to lesser compatibility and interaction with the epoxy resin.
Figure 8.5: Impact strength of HTPB-modified epoxies

The decreasing tendency of impact strength after an optimum level of 10 phr rubber inclusion is attributed to the aggregated size of rubber particles as the concentration of rubber increases. Similar behavior has also been reported in other rubber-modified epoxy systems [17-18]. The large elastomeric domains act as deflection sites and lead to catastrophic failure of matrix. However, matrix ductility and reduction in cross-linking density attained by the incorporation of rubber is responsible for the improvement of impact strength of the high rubber content blend in comparison to that of neat epoxy. The influence of matrix ductility on impact strength behavior has been well explained in certain rubber-modified epoxy works [19-20]. The improvement in impact strength shall be correlated with toughness enhancement. The impact strength measurement is very sensitive to imperfections of the specimens. Imperfections due to voids, bubbles, and inclusions may affect the results of impact strength. For an unnotched specimen, stress may not
concentrate on a specific point and the material undergoes fracture at the weakest point. So normally impact strength of samples may not be complementary to that of tensile test results.

With a view to investigate the relation between cure temperature and impact strength, a modified sample containing 10 weight % HTPB has been investigated. This is depicted in Fig. 8.6.

**Figure 8.6:** Impact strength of HTPB-modified epoxies cured at different temperatures

The Figure demonstrates that the impact strength of modified epoxy networks increased slowly and attained a maximum at 160°C. A comparatively lower value was noted for a high temperature cured sample. The morphology of samples at a high $T_{\text{cure}}$ was found to be noticeably different from that of a low temperature cured one and this morphological difference shall be a parameter which influenced the impact nature. The morphology of the modified epoxies cured at 160 and 200°C are
portrayed in Fig. 8.7 (a) and (b) respectively. Well defined domains of particles having a bimodal size distribution are clearly observable in the SEM photograph of the blend cured at 160°C which was found to be the optimum cure temperature. Whereas, in the blend of the same composition, but $T_{\text{cure}} = 200^\circ\text{C}$, domain distribution was not well characterized. This shall be attributed to the fact that phase separation started well before gelation, and since high temperature leads to fast curing, particle growth was not effective due to restriction caused by diffusion in the epoxy matrix. Well distributed particles in the matrix can build up better energy dissipation which leads to significant impact behavior of the matrix. Similar results are reported in the case of elastomer-modified epoxies [21] and thermoplastic toughened epoxies [22].

Thus the sample cured at 200°C was unable to accomplish a developed phase separated morphology due to speedy reactions and insufficient time which ultimately resulted in the single phase morphology on the fracture surface which is accounted for its poor impact performance. It is widely accepted that the presence of well distributed phase separation of elastomer domains is a necessary criterion for toughening in rubber-modified epoxies. However, compared to the neat epoxy matrix the high
temperature cured network showed greater toughness and impact strength. This is ascribed to the shear deformation of fracture surface of the modified network, unlike the unmodified one. The ductility of the modified matrix imparts absorption of energy, which ultimately leads to toughness characteristics [23].

Fig. 8.8 depicts the flexural properties of neat and HTPB-modified resin samples. The flexural strength and modulus of the modified samples were lower than that of the unmodified epoxy. The phase separated low modulus rubber domains imparted reduction in modulus. A very small amount of rubber may got incorporated into the epoxy matrix, and thereby decreased the modulus of the thermoset network. The rubber that was incorporated into the resin matrix is responsible for the reduction in flexural strength of the modified samples. Previous works on rubber-modified epoxies support this observation [24-28].

Figure 8.8: Flexural properties of neat and HTPB-modified epoxies.
8.1.3 Fracture toughness properties of epoxy-rubber blends

Epoxy-CTBN systems

Since toughness enhancement is the main objective of elastomeric modification, experimental methods of quantifying improvements in toughness have received considerable attention. Most of the recent advances in the understanding of epoxy fracture have been through the application of fracture mechanics, whereby quantifiable expressions of toughness such as the critical stress intensity factor (fracture toughness), $K_{IC}$, and critical strain energy release rate (fracture energy), $G_{IC}$, are frequently quoted. The values were determined on single edged notched SEN-T specimens as per expressions 2.17 and 2.19 respectively, mentioned in chapter 2. Fig. 8.9 graphically illustrate the effect of elastomer concentration on fracture energy, $G_{IC}$ and fracture toughness, $K_{IC}$.

![Figure 8.9: Fracture properties of epoxy-CTBN blend systems](image-url)
Fracture energy, $G_{IC}$, increased dramatically with relatively small increase in rubber concentrations and eventually resulted in a maximum toughness value at a CTBN concentration of at 15 weight %. Further increase in rubber concentration led to reduction in $G_{IC}$. A similar trend was observed in the value of fracture toughness, $K_{IC}$, also. The enhancement in fracture energy and toughness were related to changes in morphological character [29-30]. When the rubber concentration was below about 20 weight %, SEM revealed particulate morphological characteristics with evidence of small inclusions of elastomer, having an average size of 0.5-1µm in diameter. These elastomeric particles which were well dispersed and adhered to the matrix caused sufficient stress transfer within the cross-linked matrix and were responsible for the improvement of properties. As the volume fraction of the dispersed rubbery phase (VD) increased, toughness also improved. But the modulus and yield stress decreased slightly. Initially the fracture energy increased with respect to the volume fraction. But after attaining a maximum for 15 weight %, it decreased slightly. This may be due to the flexibilization of the epoxy matrix by dissolution of rubber, the property which is not recommendable for toughness enhancement. A still higher concentration of CTBN will contribute to plasticization effect. Interfacial area was higher, to a certain extent, for larger percentage distribution of CTBN. But this cannot be logically correlated with $G_{IC}$.

**Epoxy-HTPB systems**

Changes in the values of $K_{IC}$ and $G_{IC}$ as a function of HTPB weight % are furnished in Fig. 8.10. Pre-reaction of the rubber with the hardener imparts interaction between rubber particles and epoxy matrix during curing. The addition of rubber imparted an increase in the value of $K_{IC}$ up to an optimum rubber content of 10 phr. Fracture energy also showed a similar trend. No
further increase was found noticeable on further loading of rubber. This shall be attributed to the agglomeration of rubber particles at higher concentrations.

Figure 8.10: Fracture toughness properties of HTPB-modified epoxies

Since fracture toughness properties are closely related to morphological characteristics, a detailed description and correlation between them were given in chapter 2 under “Morphology of HTPB-modified epoxies.” Flexibilization to a lower extent and reduction in cross-linking density was responsible for the toughness improvement in these systems.

The fracture toughness behavior of CTBN-epoxy samples was superior when compared to that of HTPB samples having the same composition. Once again, this explains, the superior energy transfer mechanism operating in CTBN-modified epoxies which became possible due to the excellent interfacial adhesion and bonding with the matrix. Even though such strong interfacial adhesion was lacking in HTPB-epoxy samples, the reduction in cross-linking density and incorporation of the elastomer into
the matrix, at least to a slight extent, is accountable for the enhancement of the fracture properties.

### 8.1.4 Heat deflection temperature

The heat deflection temperature or heat distortion temperature (HDT) is an additional measurement parameter and is defined as the temperature at which a polymer sample deforms under a specified load. This property of the material is applied in many aspects of product design, engineering, and manufacture of products. HDT is dependent on the applied load, specimen geometry, heating rate, and the chosen flexure value and hence the value allows different materials to be compared with one another.

The variations of HDT in CTBN and HTPB-modified epoxies are represented in Table 8.3 and 8.4 respectively. HDT was higher for neat epoxy sample and the value decreased with the inclusion of elastomers. This is assigned to the low modulus characteristics of elastomers. However, the modified epoxy blends can withstand up to a reasonable temperature without distortion. Epoxy-CTBN systems observed slightly lower heat deflection temperatures.

**Table 8.3: Heat deflection temperature of different CTBN systems**

<table>
<thead>
<tr>
<th>Epoxy-CTBN systems</th>
<th>Heat deflection temperature (°C)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>140</td>
<td>±2</td>
</tr>
<tr>
<td>5 phr</td>
<td>135</td>
<td>±1</td>
</tr>
<tr>
<td>10 phr</td>
<td>126</td>
<td>±2</td>
</tr>
<tr>
<td>15 phr</td>
<td>122</td>
<td>±2</td>
</tr>
<tr>
<td>20 phr</td>
<td>115</td>
<td>±3</td>
</tr>
<tr>
<td>25 phr</td>
<td>108</td>
<td>±2</td>
</tr>
</tbody>
</table>
Table 8.4: Heat deflection temperature of different HTPB systems

<table>
<thead>
<tr>
<th>HTPB systems</th>
<th>Heat deflection temperature (°C)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>140</td>
<td>±3</td>
</tr>
<tr>
<td>5 phr</td>
<td>136</td>
<td>±2</td>
</tr>
<tr>
<td>10 phr</td>
<td>127</td>
<td>±1</td>
</tr>
<tr>
<td>15 phr</td>
<td>124</td>
<td>±2</td>
</tr>
<tr>
<td>20 phr</td>
<td>116</td>
<td>±2</td>
</tr>
</tbody>
</table>

8.1.5 Hardness

The hardness of the CTBN blends was measured by ball-indentation method. Hardness values showed a decreasing trend as the rubber concentration increased. The inclusion of rubber caused reduction in modulus of the cross-linked network owing to the amalgamation of more elastomer into the epoxy matrix (Fig. 8.11).

Figure 8.11: Ball-indentation hardness of CTBN-modified epoxies
The hardness of HTPB-modified epoxies also displayed a similar decreasing trend [Fig.8.12]. Low modulus elastomeric phase caused reduction in cross-linking density of the system by occupying the space in between the reaction sites. The reduction was more prominent in CTBN samples than in HTPB samples. This is due to the better interaction of CTBN elastomer with epoxy resin matrix than that of the HTPB rubber.

![Graph: Hardness vs Weight % of HTPB](image)

**Figure 8.12:** Ball-indentation hardness of HTPB-modified epoxies

### 8.1.6 Instrumented falling weight impact tests

Instrumented falling weight impact (IFWI) tests were performed on epoxy-CTBN/HTPB blend samples and the corresponding values of perforation energy (total energy/thickness) are recorded in Table 8.5.
Table 8.5: Perforation energy from IFWI tests

<table>
<thead>
<tr>
<th>Rubber weight %</th>
<th>CTBN</th>
<th>HTPB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Perforation energy [J/mm]</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.41 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.46 ± 0.17</td>
<td>0.43 ± 0.05</td>
</tr>
<tr>
<td>10</td>
<td>0.53 ± 0.12</td>
<td>0.46 ± 0.08</td>
</tr>
<tr>
<td>15</td>
<td>0.50 ± 0.13</td>
<td>0.39 ± 0.12</td>
</tr>
<tr>
<td>20</td>
<td>0.47 ± 0.07</td>
<td>0.35 ± 0.09</td>
</tr>
</tbody>
</table>

The values of perforation energy increased with the inclusion of rubber and reached to a maximum at 10 phr rubber concentration. Further increase in the concentration of elastomers decreased the perforation energy in both epoxy-elastomer blends.

Nanoindentation Analyses

8.2 Load-displacement behavior of epoxy-CTBN/HTPB blend samples

Fig. 8.13 (a) and (b) show the typical loading-hold-unloading profiles of neat epoxy and the elastomer blend systems under a maximum load of 100 mN. It was observed that with the same loading condition, resistance to indentation force and indentation depth at 100 mN, both before and after the maximum hold segment, varied from sample to sample. The incorporation of different weight % of rubber shifted the load-displacement curves. The highest indentation load at the same depth was noted for neat epoxy.

It was also noticed that the slope of the initial unloading portion of the load-displacement curve changed with the weight content of liquid rubber. The slope corresponds to the material’s contact stiffness (S) which is complementary to elastic modulus (E) as per the equations (2.20) and (2.21) in chapter 2. It followed that the hardness and the elastic moduli of samples would consequently be changed by varying CTBN/HTPB concentration.
Figure 8.13: (a) Load-displacement profiles of neat epoxy and CTBN blends

Figure 8.13: (b) Load-displacement profiles of neat epoxy and HTPB blends
8.3 Effect of rubber loading on indentation – modulus and hardness

Typical 3D representations of modulus and hardness values versus indentation position for CTBN and HTPB blends are depicted in Fig. 8.14 (a), (b), (c) and (d). Different colors on the graph indicate different values for modulus and hardness. For the modulus curve all the values were included between 3, and 5. Similarly all the values between 0.3 and 0.4 were considered for the hardness representation. Thus by noting the color on the graph one can recognize the corresponding value of modulus and hardness. It may be noted that only few colors of the scale were used on the graphs for convenience. The overall idea that the graphs conveyed was the three dimensional vision of the nanoindentation measurement and the corresponding values of modulus and hardness. The values showed a decreasing trend due to elastomer amalgamation with epoxy matrix.

![Modulus Vs indentation position](image)

**Figure 8.14 (a)** Modulus versus indentation position (epoxy-CTBN blends)
Figure 8.14(b) Hardness versus indentation position (epoxy-CTBN blends)

Figure 8.14(c) Modulus versus indentation position (epoxy-HTPB blends)
Figure 8.14(d) Hardness versus indentation position (epoxy-HPB blends)

Fig. 8.15: (a) and (b) represents the changes in modulus and hardness of the epoxy matrix as rubber inclusion increases. It may be noted that the 3D representations and these Figures are drawn from two different indentation tests, out of a number of tests performed.
Figure 8.15: (a) Modulus and hardness versus CTBN concentration

Figure 8.15: (b) Modulus and hardness versus HTPB concentration
All indentation tests clearly showed that both of these properties decreased with the addition of the elastomeric phase. The low modulus elastomers can reduce the modulus and hardness of the epoxy network structure. However, this reduction was more prominent in CTBN-modified samples. For instance, the inclusion of 10 phr CTBN registered 8 and 14% reduction in modulus and hardness, whereas for HTPB addition, the corresponding values were only 3 and 7, respectively. The miscibility of CTBN in epoxy, to a certain extent, substantiates this.

The advantage of nanoindentation technique is that the behavior of the material due to its localized nature can be studied and hence the measurement is sharper and precise. Also, a very small sample volume is adequate and offers an exclusive prospect to assess changes in mechanical behavior. The conventional tensile test, on the other hand, provides information regarding the heterogeneity of the material and hence the bulk property is measured. This is certainly a disadvantage and caused errors in the value of tensile results if the material is imperfect due to micro-voids and poor dispersion.

Hardness value signifies the material’s resistance power to the local surface deformation. Permanent deformation of a thermoset based blend leads to rupture of the polymer network or relative slipping between the heterogeneous phases. The lowering of hardness with the inclusion of CTBN is assigned to the segregation of the phase separated domains as well as dissolution of CTBN into the epoxy matrix. In epoxy-HTPB blends, this effect may be primarily due to the reduction in cross-linking density. Thus the elastomeric phase tends to put forth a comparatively lower resistance to deformation and thus defend the material from crack-failure.

It is to be noted that no regular trend was observed in the reduction of modulus or hardness by the incorporation of elastomer. This shall be attributed to the unpredictable distribution of elastomer domains in the
epoxy matrix. The reduction in the value became more noteworthy, in either case, when the elastomer concentration becomes higher say, 20 and 25 phr. At a higher concentration of rubber phase, the parameters of phase separated particles such as number, size, and volume average domain diameters became more predominant and brought about reduction in the modulus of the epoxy network. In addition to this, some dissolved rubber (more applicable to CTBN) might have flexibilized the epoxy matrix. Phase separation of bigger particles took place (in both cases) when the concentration of rubber phase increased. The size of the dispersed particles and their contribution to mechanical properties are related [31]. Enhancement of mechanical properties was more pronounced when the dispersed particles are homogeneous and are having a size distribution of approximately 1-2 μm.

In order to understand the correlation between the properties and deformation of the matrix, the modulus and hardness of neat epoxy and its blends with 5 and 25 phr of CTBN/HTPB at different maximum loads (corresponding to four indent depths) were noted. Fig. 8.16 (a), (b), (c) and (d) depict the observation. Both hardness and modulus showed relatively higher values with 1mN as the maximum load than those with other loading conditions. The indentation depth at this load was less than 500 nm, the higher modulus and hardness values might be due to the surface uncertainties such as roughness in the top surface level as well as the indentation size effect (ISE) [32-34]. The indentation size effect could be due to the blunting of the indenter tip at apex, which leads to an overestimate of the hardness and modulus near-surface area. The modulus and hardness become stabilized after a certain depth with further increase in the maximum load. This is because of the minimization of uncertainties when indentation depth exceeds 2–3 μm deep into the surface.
Figure 8.16: (a) Modulus versus displacement into surface for neat and CTBN-modified epoxies

Figure 8.16: (b) Hardness versus displacement into surface for neat and modified epoxies
Figure 8.16: (c) Modulus versus displacement into surface for neat and HTPB-modified epoxies

Figure 8.16: (d) Hardness versus displacement into surface for neat and HTPB-modified epoxies
Similar observations were noted in the investigation of mechanical properties of epoxy-organoclay nanocomposites by nanoindentation technique [35]. In the present case, a regular trend in these properties was not evident. This could probably be credited to the unpredictability in the distribution of elastomeric domains in the matrix that were subjected to nanoindentation.

8.4 Fracture behavior

Fracture toughness at small scales can be measured by indentation technique [36-38]. A simple correlation between fracture toughness and radial cracks has been put forward by Lawn et al. [39] as given below:

\[
K_{ic} = \alpha \left( \frac{E}{H} \right)^{\frac{1}{2}} \left( \frac{P}{C^{\frac{1}{3}}} \right) \quad \text{----------------- (8.1)}
\]

In this equation \( \alpha \) is an empirical constant which depends on the geometry of the indenter and \( P \) is the peak indentation load corresponding to the radial crack length, \( C \) formed by indentation on the surface of the brittle thermoset matrix. The term \( \left( \frac{P}{C^{\frac{1}{3}}} \right) \) represents the capability of the material to resist the crack propagation which can be explained by crack-bridging mechanism [40-41], one of the important toughening mechanisms in toughened epoxies. The ratio of \( \frac{E}{H} \) is a static property of the material denoted by the potential of the material to fracture tendency. The overall stiffness of the material is represented by the elastic modulus \( E \) whereas cohesive energy density [42], which is affected by the cross-linking density is represented by the term hardness \( H \). Both stiffness and cross-linking density are affected by the inclusion of liquid rubber into the epoxy matrix. The occupancy of liquid rubber between the cross-linking sites of the epoxy network reduced the cross-linking density. The reduction in modulus was significant at a higher weight content of
liquid rubber. As mentioned previously, the modification of epoxy network with a low weight % of elastomers, in fact, reinforced the matrix due to the interaction of the reactive carboxyl functionality with the epoxy resin, thereby extending the dimensionality of the epoxy matrix. Thus the phase separated rubber domains were well adhered to the matrix and they acted as stress concentrators leading to the reinforcement of the matrix. The enhancement in the impact strength of 5 and 10 phr rubber-modified epoxies were clear evidence for this. But when the elastomer concentration was comparatively higher flexibilization of the matrix took place which ultimately reduced the modulus of the network (more appropriate to CTBN). Agglomeration of rubber particles also adds to this behavior. The reduction in $T_g$ of the network is a signature of this behavior [43]. In HTPB-modified samples, the diminution in the modulus is attributed to the reduction of cross-link density of the matrix on adding higher weight % of rubber. The ratio of $\frac{E_f}{H}$, represents the synergy of these effects. It was observed that the ratio increased upto 10 weight % of CTBN and afterwards showed a slow decline. Similar analysis, but contradictory observations are reported elsewhere. In a work done by Shen et al. [35] where epoxy-nanoclay composite was the subject of analysis, the ratio of $\frac{E_f}{H}$ with varying % of clay monotonically increased with clay loading. This is in concurrence with the expectations since clay particles increase the modulus of epoxy network.

In the present study, impact strength has been used to represent the fracture toughness property of the rubber-modified epoxies as the property is also a signature of fracture toughness behavior [44]. High impact strength values were generally obtained for materials having higher fracture toughness characteristics. Figs. 8.17 (a) and (b) depict impact strength and $\frac{E_f}{H}$ values as a function of weight content of CTBN and HTPB respectively.
The properties of both blend systems showed a similar trend. Thus it was interesting to observe that the ratio of $\frac{E}{H}$ showed a similar trend to the impact strength values in both elastomers modified systems. Therefore, the approach suggested above by correlating the ratio of indentation modulus to hardness with the conventional impact strength to evaluate the fracture toughness characteristics (without destructing the materials) is acceptable in rubber-modified epoxies.

Figure 8.17: (a) Impact strength and $\frac{E}{H}$ values as a function of weight content of CTBN
8.5 Conclusion

The bulk mechanical properties of CTBN/HTPB rubber-modified epoxy samples were determined. The neat epoxy system underwent a brittle failure, whereas the CTBN samples registered a ductile fracture. This is due to the miscibility of the elastomer in epoxy, which was more prominent in samples containing higher weight % of CTBN. The reduction in the values of tensile strength and modulus also signified this. On the other hand, the ductility behavior in HTPB-samples was less than that of CTBN counterparts. The samples, in general, experienced brittle nature of failure. This behavior was due to the lesser miscibility nature of HTPB rubber than CTBN in epoxy. This rationalized the tensile properties of the samples. The reduction in tensile strength and modulus were also comparatively less than epoxy-CTBN samples. The incorporation of CTBN in the range of 10-15 weight %, and HTPB to an extent of 10 weight % has improved the impact strength of the cured matrix. Higher impact strength was noted for CTBN samples. Flexural

Figure 8.17: (b) Impact strength and $\frac{E}{H}$ values as a function of weight content of HTPB
properties reduced with the incorporation of elastomers. More prominent fracture toughness characteristics were shown by CTBN-epoxy blends having 10-15 phr CTBN content and were explained by the morphology of the systems. Some of the toughening mechanisms prevailing in rubber toughened epoxies were discussed. Heat deflection temperature and hardness of blend samples decreased with the inclusion of elastomers and the reduction was more prominent in CTBN-modified epoxies. This was due to the higher interaction of low modulus CTBN elastomer with the epoxy matrix than the HTPB rubber.

Finally, nanoindentation technique has been employed to identify the localized mechanical properties of the elastomer-modified samples. Both systems experienced diminution in modulus and hardness. However, CTBN-modified epoxies registered highest reduction which was accredited to the high interaction of the elastomer with the resin matrix. The technique was also used to evaluate the fracture behavior of the rubber-modified epoxies. The methodology was based on the comparison of the ratio of indentation modulus and hardness, $E/H$, with conventional impact strength measurement. The non-destructive nature of the nanoindentation technology has always been advantageous over the conventional mechanical testing methods. It was observed that both the ratio of $E/H$ and impact strength of CTBN/HTPB systems showed the same trend, but to different extents. The values of both methods were maximum for samples in the range of 10-15 phr CTBN and for 10 phr HTPB concentration and thereafter declined. The impact strength enhancement is based on the morphology development which ultimately determined the toughness characteristics. It was established that the nanoindentation methodology to scrutinize the fracture toughness property was well in agreement with the conventional mechanical testing method.
References

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