Chapter 5

Effect of Nanoclay Concentration on Morphology and Ultimate Properties of Epoxy/Clay/CTBN Nanocomposites

This chapter deals with a systematic study conducted to investigate the polymer and polymer/blend properties resulting from the introduction of nanoclay (1-3 phr) into epoxy and epoxy/CTBN blend. The morphological characterization of nanocomposites was carried out using X-ray diffraction and microscopic (SEM and TEM) techniques. DMA was used to study the viscoelastic properties of the nanocomposites as a function of clay concentration and then correlated with the morphology. The flexural and tensile properties of the nanocomposites were also studied. It was found that the clay nanostructure and distribution among the blend component affect both viscoelastic and mechanical properties of the epoxy/clay/CTBN nanocomposite. Moreover, fracture toughness and impact properties of nanocomposites were studied as a function of clay loading. TGA was carried out to study the thermal behaviour of the prepared nanocomposites. The thermal degradation parameters of epoxy/clay/CTBN nanocomposite were found to depend mainly on the dispersion of clay rather than its distribution among the blend component.

Parts of the results of this chapter have been communicated to ‘RSC Advances’ for publication.
5.1. Introduction

Epoxy resins exhibit some outstanding properties such as high modulus, high chemical resistance and high dimension stability. With the general goal of improving epoxy performance, reinforcement with nanoscale fillers currently represents an active field of research for advanced high-performance applications.\textsuperscript{1-6} Among the inorganic materials used as fillers to improve the properties of polymers, organically modified layered silicates, such as MMTs, have recently received a great deal of attention.\textsuperscript{7-11} The challenge is to fully understand how to destroy the layered structure of the MMT within a given matrix, so that the polymer can be said to be truly ‘nanoreinforced’ and the properties, tailored and optimized.

During the processing stage of epoxy/clay nanocomposites, resin and hardener molecules can diffuse into the clay galleries and react within the interlayer space leading to intercalated structures. The polymerisation reactions within the galleries may also lead to the complete separation or delamination of nanoclay platelets into individual layers encapsulated by polymer molecules forming the so-called exfoliated structures. Park and Jana\textsuperscript{12} studied the mechanism of exfoliation of nano clay in epoxy/clay nanocomposites. The elastic force exerted by the cross-linking epoxy molecules inside the clay galleries push out the outermost clay layers from the tactoids against the opposing forces arising from electrostatic and van der Waals attraction. Various parameters like cure temperature, mixing method, surfactant chemistry, clay volume fraction, nature of the curing agent affect the microstructure and hence properties of the epoxy/clay nanocomposites.\textsuperscript{13-17} The crucial role of interface in determining the properties of epoxy/clay nanocomposites was studied by Zaman et al.\textsuperscript{18} The chemical reaction of clay modifier with epoxy created a strong interface, resulting in the best
dispersion of clay layers and the higher increment of young’s modulus, fracture toughness and thermal property.

The emerging interest in polymer matrix based nanocomposites leads to the concept of incorporating both toughening material and nanofiller into epoxy, to generate polymeric material with remarkable properties. The use of both liquid rubber and nanoclay were widely reported as an effective way to make epoxy tough and stiff.\textsuperscript{19-23} The overall performance of this complex nanocomposite depends on various factors such as –effect of clay on rubber phase separation, effect of CTBN on clay intercalation/exfoliation and localization of clay among the blend components.

The present chapter addresses the nanostructure development in epoxy/clay and epoxy/clay/CTBN nanocomposites as a function of clay loading. The influence of nanostructure morphology on the mechanical, viscoelastic and thermal properties of epoxy/clay and epoxy/clay/CTBN nanocomposites were studied in detail.

5.2. Result and Discussion

5.2.1. Effect of nanoclay concentration on morphology of epoxy/clay and epoxy/clay/CTBN nanocomposites

The wide-angle XRD was used to determine the d spacing of clay platelets in epoxy/clay and epoxy/clay/CTBN nanocomposites. The XRD patterns for nanoclay (I.28E), epoxy/clay and epoxy/clay/CTBN nanocomposites with different clay loading are shown in Fig.5.1. The [001] diffraction of I.28E clay layers appears at $2\theta = 3.64$ corresponding to the basal spacing 24.5Å. For epoxy/1 phr clay nanocomposite, the lack of any diffraction peak as opposed to the diffraction peak at $2\theta = 3.64$ for nanomer I.28E, indicates the possibility of having exfoliated silicate nanolayers of organophilic clay dispersed in the epoxy matrix. For epoxy/2 phr clay nanocomposites the
presence of a prominent diffraction peak at 2θ = 3.26, indicates an intercalated structure with a ‘d’ spacing of 27.05 Å. However, a prominent diffraction peaks is absent in 3 phr clay loaded epoxy nanocomposite. A remnant shoulder at 2θ=2.36 indicates that a part of the clay is intercalated with a d spacing of 35.94 Å. The remnant shoulder and small peaks in XRD curve of 3 phr clay loaded system indicate that nanoclay is not uniformly distributed in the epoxy matrix. A similar trend in ‘d’ spacing was shown by epoxy/clay/CTBN nanocomposites. The XRD pattern of epoxy/clay/CTBN nanocomposite with 1 phr clay does not show a diffraction peak. This indicates an exfoliated silicate nanolayers of organophilic clay dispersed in an epoxy/CTBN matrix. For epoxy/clay/CTBN nanocomposite with 2 phr nanoclay, 2θ value appears at 3.19, showing an intercalated clay structure with a ‘d’ spacing of 28.25 Å. A distinct diffraction peak is absent in 3 phr clay loaded system, showing similar behaviour as that of epoxy/3 phr clay nanocomposites. A remnant shoulder at 2θ =2.04 shows the presence of a portion of intercalated clay with a ‘d’ spacing of 43.26 Å. It was noted that the epoxy/clay/CTBN nanocomposite shows a higher ‘d’ spacing than epoxy/clay nanocomposite having same amount of nanoclay. Such an effect was reported earlier by Lee et al. 22 in jeffamine cured epoxy-clay nanocomposites toughened with a CTBN. The functional end groups of liquid rubber must play an important role in the clay exfoliation process.24-26 The CTBN preferentially interact with nanoclay in epoxy/CTBN blend (details in chapter 4).The low molecular weight CTBN interpenetrated into the clay galleries in epoxy/clay/CTBN nanocomposite due to this preferential interaction.
Figure 5.1  XRD plots for organically modified clay (I.28E), epoxy/1-3 phr clay nanocomposite and epoxy/1-3 phr clay/15 phr CTBN nanocomposites

In order to have a clear visualization of the nanocomposite microstructure, TEM images of the samples were analyzed. The TEM micrographs of epoxy/clay and epoxy/clay/CTBN nanocomposites with different clay loading are shown in Fig.5.2.
Figure 5.2 TEM images of epoxy/clay nanocomposite with (a) 1 phr (b) 2 phr (c) 3 phr nanoclay and epoxy/clay/CTBN nanocomposite with (d) 1 phr (e) 2 phr (f) 3 phr nanoclay.

Both epoxy and epoxy/CTBN matrix with 1 phr clay have fully delaminated clay layers giving rise to fully exfoliated nanocomposite, consistent with the XRD results. However, 2 phr clay loaded epoxy/clay and epoxy/clay/CTBN nanocomposites have intercalated morphology with partial exfoliation. However, the extent of exfoliation is higher in the ternary system. The clay structure in 3 phr loaded epoxy and epoxy/CTBN matrix is similar to that in 2 phr loaded systems. However, some extent of tactoids is visible in micrographs taken from different region of nanocomposites having 3 phr clay. Using high resolution TEM, it was difficult to spot the microsized CTBN phase, which was dispersed in epoxy. Hence, in order to examine the micro phase along with nanoclay distribution, the fracture surfaces of nanocomposites were studied using SEM.
Fig. 5.3 a–h displays some representative SEM images of the fracture surfaces of epoxy/clay and epoxy/clay/CTBN nanocomposites prepared with the different loading of clay. The surface of the pure epoxy samples was smooth and featureless, representing brittle failure of homogenous materials. The epoxy/CTBN blend has two distinct phases – a continuous epoxy matrix and the dispersed rubber phase. The dispersed CTBN particles were etched out from the samples by using toluene leaving micro cavities (Fig. 5.3e, 5.3f, 5.3g and 5.3h). The fracture surface of the clay filled epoxies (Fig. 5.3b, 5.3c and 5.3d) show considerable roughness. Epoxy/1 phr clay nanocomposites (Fig. 5.3b and 5.3f) have well defined fracture margins which represents a good adhesion between the matrix and clay platelets. The interface quality decreases with increase in clay loading. At higher concentration (3 phr) (Fig. 5.3d and 5.3h) a poor adhesion exists between the agglomerates and the resin. The fracture surfaces of epoxy/CTBN/clay nanocomposites show both the characteristics of epoxy/CTBN and epoxy/clay nanocomposite. At higher magnification of epoxy/1 phr 1.28E/15phr CTBN (inset in Fig. 5.3f), the cavity created after the etching of CTBN domains discloses small scales like structures, indicating the presence of trapped clay platelets inside the phase separated CTBN. Highly delaminated individual clay platelets easily get inside the phase separated CTBN phase than intercalated platelets. The presence of clay platelets inside the phase separated CTBN increases CTBN domain size (Dn~1.7µm) when compared with its domain size (Dn~1.2µm) in epoxy/CTBN blend. However, the intercalated clay layers in 2 and 3 phr clay loaded epoxy/clay/CTBN nanocomposites located in the epoxy matrix with a tendency to align near the phase separated CTBN phase. Clay platelets at the epoxy-CTBN interface suppress the coalescence of the rubber
particles during phase separation and resulted in lower domain size (Dn~0.82µm) of CTBN particles.

![SEM images](image1)

**Figure 5.3** SEM images of epoxy/clay nanocomposite with (a) 0 phr (b) 1 phr (c) 2 phr (d) 3 phr nanoclay and epoxy/clay/CTBN nanocomposite with (e) 0 phr (f) 1 phr (g) 2 phr (h) 3 phr nanoclay.

The morphology differences in epoxy/CTBN blend and epoxy/clay/CTBN nanocomposites having low and high amount of clay are schematically
shown in Fig. 5.4. In epoxy/1 phr clay/CTBN nanocomposites (Fig. 5.4b), most of the delaminated clay platelets reside inside the CTBN domains and hence the domain size is higher than that in epoxy/CTBN blend (Fig 5.4.a). Most of the clay platelets in epoxy/clay/CTBN nanocomposite with higher (2 and 3 phr) nanoclay loading (Fig 5.4c) locates at the epoxy-CTBN interface and it suppress the coalescence to get smaller CTBN domains compared with that in epoxy/CTBN blend.

![Figure 5.4 Schematic diagram showing the morphological difference in (a) epoxy/CTBN blend (b) epoxy/clay/CTBN nanocomposite with low (1 phr) nanoclay loading (c) epoxy/clay/CTBN nanocomposite with higher (2 and 3 phr) nanoclay loading](image)

5.2.2. Effect of nanoclay concentration on properties of epoxy/clay and epoxy/clay/CTBN nanocomposites

5.2.2.1. Dynamic mechanical properties

Dynamic mechanical tests over a wide range of temperatures were performed to investigate the effect of clay loading on the viscoelastic properties of the epoxy/clay and epoxy/clay/CTBN nanocomposites. Fig.5.5a and 5.5b illustrate the DMA plots of storage modulus versus temperature for epoxy/clay nanocomposite and epoxy/clay/CTBN nanocomposites respectively as a function of clay loading in the temperature range from room temperature to 250°C. The storage modulus values at glassy region and rubbery region are tabulated in Table 5.1. For epoxy/clay nanocomposites, the greatest
reinforcing effect occurs near the Tg. As the chain mobility increases, the well dispersed nanoclay in epoxy can become more effective in retarding matrix molecular mobility, thus increasing the storage moduli. The nanoclay modification is more effective in strengthening soft matrix when compared to hard matrix. Similar observations were reported in the literature with various epoxy matrices.\textsuperscript{27-30} It can be seen that the storage modulus increases with increasing clay content up to 2 phr both at rubbery and glassy region. While the modulus at glassy region for epoxy/2 phr clay nanocomposite is 8\% higher than that of neat epoxy matrix, a 437\% improvement in the modulus at rubbery region is observed. Further increase in clay loading decreases the modulus. The improvement in modulus can be directly ascribed to the stiffening effect of clay fillers since the clay has a higher modulus than epoxy. It has been already reported in many epoxy/clay nanocomposites that the increments in modulus of the clay filled epoxy system were subjected to the ‘rule of mixtures’.\textsuperscript{31} The deviation of modulus value for the 3 phr clay loading, from the ‘rule of mixtures’ can be attributed to the microstructure obtained under the present processing conditions. In epoxy/clay/CTBN nanocomposites, the developed morphologies highly reflect in the dynamic mechanical properties. The magnitude of storage modulus of epoxy/CTBN blend is lower than the neat resin due to the fact that the liquid rubber flexibilizes the epoxy matrix and reduces the crosslink density.\textsuperscript{32} The dynamic mechanical behavior of 1 phr clay loaded epoxy/clay/CTBN system is different from other clay loading systems due its morphological distinctiveness. The ambient temperature modulus for 1 phr clay loaded nanocomposite is 12 \% higher than that of epoxy/CTBN blend system. However higher clay loading (2 phr and 3 phr) doesn’t cause any improvement in room temperature modulus of epoxy/clay/CTBN
nanocomposite. At the same time, the rubbery modulus of 1 phr loaded epoxy/clay/CTBN nanocomposite is 25% lower than the epoxy/CTBN blend, while 2 phr loaded system gives a 49% improvement. The possible reason which is expected to contribute for this behaviour is the following: the clay platelets inside the CTBN phase could not effectively reinforce the epoxy matrix, while the intercalated clay platelets localize in epoxy matrix could effectively do it at the rubbery state of the matrix.

Figure 5.5 Storage modulus versus temperature curves of (a) epoxy/clay nanocomposites (b) epoxy/clay/CTBN nanocomposites with different amount of clay loading. Tan δ as a function of temperature for (c) epoxy/clay nanocomposites (d) epoxy/clay/CTBN nanocomposites with different amount of clay loading.
Table 5.1 Values of storage modulus ($E'$) at rubbery and glassy region and glass transition temperature in epoxy/clay and epoxy/clay/15 phr CTBN nanocomposites.

<table>
<thead>
<tr>
<th>Clay content (phr)</th>
<th>Rubber content (phr)</th>
<th>Storage modulus ($E'$) at ambient temperature * (Pa)</th>
<th>Storage modulus ($E'$) at rubbery region **(Pa)</th>
<th>Tg (°C) of the matrix</th>
<th>Fraction of constrained region (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.96E+9</td>
<td>3.96 E+8</td>
<td>139.5</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3.21 E+9</td>
<td>1.60E+9</td>
<td>150.7</td>
<td>0.0920</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3.26 E+9</td>
<td>2.13 E+9</td>
<td>147.1</td>
<td>0.0359</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>2.97E+9</td>
<td>1.84 E+9</td>
<td>150.0</td>
<td>0.0699</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>2.67 E+9</td>
<td>1.29 E+9</td>
<td>129.6</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>3.00 E+9</td>
<td>9.49 E+8</td>
<td>115.5</td>
<td>0.0327</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>2.66 E+9</td>
<td>1.93 E+9</td>
<td>145.2</td>
<td>0.0546</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>2.66 E+9</td>
<td>1.77 E+9</td>
<td>148.5</td>
<td>0.1229</td>
</tr>
</tbody>
</table>

* 30°C
** 130°C for neat epoxy and epoxy/clay nanocomposites, 100°C for epoxy/CTBN blend and epoxy/clay/CTBN nanocomposites

Fig. 5.5c and 5.5d show tan δ as a function of temperature for epoxy/clay and epoxy/clay/CTBN nanocomposites. The glass transition temperature (Tg) values of the matrix were calculated from the peak point of highest peak in tan delta curve. The obtained Tg values for different systems are given in Table 5.1. The incorporation of nanoclay increases the Tg of the epoxy matrix. Maximum Tg value was showed with 1 phr clay loaded system (~12 °C). The increase in Tg of epoxy/clay nanocomposite is due to the hindered relaxation mobility in the polymer segment near the interface due to the chemical
bonding at the interface. The reduced interaction between clay platelets and epoxy matrix leads to the lowering of Tg in epoxy/1 phr clay/15 phr CTBN nanocomposite. Maximum Tg was obtained for 3 phr clay loading (~20 °C higher than epoxy/CTBN blend). In high clay loaded epoxy/clay/CTBN nanocomposite, the clay platelets locate in the epoxy matrix effectively increases the Tg of epoxy matrix. The height depression in tan δ peak was used to determine the amount of constrained region (macromolecular chains immobilized by the clay platelets) in epoxy/clay and epoxy/clay/CTBN nanocomposites with different clay loading (details in chapter 4). The fractions of constrained region obtained for different samples were reported in Table 5.1. Among the epoxy/clay nanocomposites, epoxy/1 phr clay has the highest fraction of constrained region; thanks to its highly exfoliated microstructure. The constrained epoxy volume in epoxy/1 phr clay/15 CTBN is lower than that of epoxy/1 phr clay nanocomposite due to lesser interaction of nanoclay and epoxy network as most of the delaminated individual clay platelets are inside the phase separated CTBN phase. In the case of epoxy/2 phr clay/15 phr CTBN and epoxy/3 phr clay/15 phr CTBN nanocomposite, the low molecular weight CTBN easily penetrated into the intercalated clay layers to expand the ‘d’ spacing, which in turn increases the fraction of constrained epoxy volume than in their respective binary nanocomposites. Fig.5.6 schematically shows the nature and extent of constrained region in epoxy/clay nanocomposite and epoxy/clay/CTBN nanocomposite having low and high amount of clay loading.
5.2.2.2. Mechanical properties

Flexural stress-strain curves of epoxy/clay and epoxy/clay/CTBN nanocomposites are given in Fig.5.7. The variation of flexural modulus and flexural strength with clay concentration is illustrated in Fig.5.8. The incorporation of clay into epoxy resin improved its flexural modulus. The improved modulus can be directly ascribed to the stiffening effect of clay fillers since the clay has a higher modulus than epoxy. The diminishing improvement in flexural modulus at high clay contents is attributed to the higher possibility of forming unwanted agglomerates, which in turn reduced the reinforcing efficiency of clay. The improvements of flexural modulus were at the expense of reductions in flexural strength as reported by others.\textsuperscript{33-35} Another possible reason for the substantial loss of flexural strength is the presence of internal stresses induced by the different cure rates between the bulk epoxy and the silicate interfaces.\textsuperscript{36}

![Diagram of constrained region in nanocomposites](image)
Figure 5.7  Flexural stress-strain curve of (a) epoxy/clay nanocomposite (b) epoxy/clay/CTBN nanocomposites with different clay loading
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As expected, the incorporation of CTBN reduces the flexural modulus of the epoxy matrix. However, the incorporation of nanoclay helps to improve the modulus. The incorporation of 1 phr nanoclay improves the flexural modulus of epoxy/CTBN blend system by 9 % and then decreases gradually with clay loading, showing a similar trend of storage modulus at ambient temperature. However, the flexural strength decreases with increase in clay loading. Even though an exfoliated clay structure is evident in epoxy/1 phr clay/15 phr CTBN system, the flexural strength doesn’t reduce dramatically as that in epoxy/1 phr clay nanocomposite. The reduced interaction between nanoclay and epoxy matrix due to the clay localization inside the rubber phase, which reduce the direct interaction of matrix with nanoclay, might be the possible reason.

Tensile stress-strain curves of epoxy/clay and epoxy/clay/CTBN nanocomposites are given in Fig.5.9. The variation of tensile properties with clay loading in epoxy/clay and epoxy/CTBN/clay nanocomposites is shown in Fig.5.10. Identical trends for flexural and tensile properties were detected for nanocomposites with different clay loading.
Figure 5.9  Tensile stress-strain curve of (a) epoxy/clay nanocomposite (b) epoxy/clay/CTBN nanocomposites with different clay loading
The effect of clay loading on the fracture toughness ($K_{IC}$) values of epoxy/clay and epoxy/clay/CTBN blends is shown in Fig. 5.11 a. It is clear from the figure that the fracture toughness of neat epoxy decreases with the incorporation of nanoclay. According to Pinnavaia the nanoclay platelets could effectively stiffen highly flexible epoxy resins than glassy epoxies. When strain is applied in the direction parallel to the surface, the clay layers will be aligned further. This strain induced alignment of the layers will enhance the ability of the particles to function as the fibres in a fibre reinforced plastics. Propagation of fracture across the polymer matrix containing aligned silicate layers is energy consuming. Due to the high glass transition temperature of the epoxy matrix (139.5 °C) used for the study, the composites were in a glassy state at room temperature. In a glassy matrix, clay particle alignment upon applied strain is minimal and blocking of the fracture by the exfoliated clay is less efficient and resulted in the lower $K_{IC}$ values for the epoxy/clay nanocomposite. The presence of 15 phr CTBN effectively increases $K_{IC}$ to 34.5 %. But the incorporation of nanoclay into
epoxy/CTBN blend decreases the $K_{IC}$. It should be worth noted that the fracture toughness values of epoxy/clay/CTBN nanocomposites with low clay loading (1, 2 phr) are higher than that of neat epoxy. However at a higher clay loading (3 phr), the $K_{IC}$ value is slightly lower than that of neat epoxy. The variation of charpy impact strength with clay loading of epoxy/clay and epoxy/CTBN/clay nanocomposites is shown in Fig.5.11.b. A similar trend in fracture toughness and impact strength is detected in both epoxy/clay and epoxy/clay/CTBN nanocomposites.

Falling weight impact measurements were carried out to study the impact resistance of the epoxy/clay and epoxy/clay/CTBN nanocomposites and the results are tabulated as a function of clay loading in Table 5.2. Neat epoxy and all the epoxy/clay nanocomposites did not pass the falling weight impact resistance test under 2.5 kg load. The epoxy/15 phr CTBN blend and epoxy/clay/15 phr CTBN nanocomposites containing low amount of nanoclay i.e. 1 and 2 phr passed the impact resistance test. However the
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epoxy/clay/15 phr CTBN nanocomposite with higher clay loading (3 phr) failed the impact resistance test.

Table 5.2  Impact resistance performance of epoxy/clay and epoxy/clay/CTBN nanocomposites with different amount of nanoclay.

<table>
<thead>
<tr>
<th>Clay content (phr)</th>
<th>Rubber content (phr)</th>
<th>Impact Resistance (2.5kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0</td>
<td>0</td>
<td>Did not pass</td>
</tr>
<tr>
<td>1 0</td>
<td>0</td>
<td>Did not pass</td>
</tr>
<tr>
<td>2 0</td>
<td>0</td>
<td>Did not pass</td>
</tr>
<tr>
<td>3 0</td>
<td>0</td>
<td>Did not pass</td>
</tr>
<tr>
<td>0 15</td>
<td></td>
<td>Pass</td>
</tr>
<tr>
<td>1 15</td>
<td></td>
<td>Pass</td>
</tr>
<tr>
<td>2 15</td>
<td></td>
<td>Pass</td>
</tr>
<tr>
<td>3 15</td>
<td></td>
<td>Did not pass</td>
</tr>
</tbody>
</table>

5.2.2.3. Thermal properties

The TGA and differential thermogravimetric (DTG) curves of the epoxy, I.28E clay, CTBN, epoxy/clay nanocomposite and epoxy/clay/CTBN nanocomposites with varying amount of clay at 10°C/min under nitrogen are shown in Fig.5.12. Table 5.3 tabulates the thermogravimetric data, including $T_{10\%}$, $T_{80\%}$ of degradation and the residual not volatile material left at 700 °C. $T_{10\%}$ is the onset temperature at which 10% degradation of the system occurs and $T_{80\%}$ is the temperature at which 80 % degradation occurs. The temperature of the maximum weight loss rate ($T_{\text{max}}$) of samples, obtained from the DTG curves is also shown in Table 5.3.
Figure 5.12. (a) TGA (b) DTG thermograms of epoxy, L28E clay and CTBN (c) TGA (d) DTG thermograms of epoxy/clay nanocomposites with different amount of clay (e) TGA (f) DTG thermograms of epoxy/15 phr CTBN blend and epoxy/clay/15 phr CTBN nanocomposites with different amount of nanoclay
### Table 5.3 Thermogravimetric properties of epoxy, CTBN, I.28E nanoclay, epoxy/clay and epoxy/clay/15 phr CTBN nanocomposites with different clay loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$T_{10%}$ (°C)</th>
<th>$T_{80%}$ (°C)</th>
<th>Residual weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>408.33</td>
<td>340.27</td>
<td>495.88</td>
<td>16.20</td>
</tr>
<tr>
<td>CTBN</td>
<td>467.22</td>
<td>401.16</td>
<td>474.60</td>
<td>1.22</td>
</tr>
<tr>
<td>I.28E clay</td>
<td>317.36 (1st step) 280.98*</td>
<td>423.61 (2nd step) *</td>
<td>64.27</td>
<td></td>
</tr>
<tr>
<td>Epoxy/1 phr I.28E</td>
<td>412.00</td>
<td>362.58</td>
<td>666.09</td>
<td>19.76</td>
</tr>
<tr>
<td>Epoxy/2 phr I.28E</td>
<td>409.08</td>
<td>356.83</td>
<td>618.28</td>
<td>19.30</td>
</tr>
<tr>
<td>Epoxy/3 phr I.28E</td>
<td>407.13</td>
<td>345.64</td>
<td>**</td>
<td>26.42</td>
</tr>
<tr>
<td>Epoxy/15 phr CTBN</td>
<td>406.52</td>
<td>328.38</td>
<td>465.87</td>
<td>14.81</td>
</tr>
<tr>
<td>Epoxy/1 phr I.28E/15 phr CTBN</td>
<td>415.13</td>
<td>368.68</td>
<td>493.10</td>
<td>16.51</td>
</tr>
<tr>
<td>Epoxy/2 phr I.28E/15 phr CTBN</td>
<td>412.77</td>
<td>369.86</td>
<td>491.61</td>
<td>16.34</td>
</tr>
<tr>
<td>Epoxy/3 phr I.28E/15 phr CTBN</td>
<td>408.33</td>
<td>327.35</td>
<td>492.58</td>
<td>16.57</td>
</tr>
</tbody>
</table>

* Only 35.66% degraded
** Only 73.52% degraded

I.28E nanoclay degraded in a two-step process leaving 35.7% of the inorganic silicates at around 700 °C. Thermal decomposition of organic modifier (trimethyl stearyl ammonium) between silicate layers is responsible for the first peak in the range 200-330 °C. The initial onset degradation temperature ($T_{10\%}$) and maximum degradation temperature ($T_{\text{max}}$) of CTBN rubber is higher than neat epoxy. However the residual weight after complete degradation is nearly zero for CTBN while 16.2 % remains after the
complete degradation of epoxy. Because inorganic substances have good thermal stability, it is generally believed that the introduction of layered silicate platelets into organic materials can improve their thermal stability. This is because, not only clay platelets act as a heat barrier in the early stages of thermal decomposition, but they also slow down the volatilization due to the labyrinth effect they create in the polymer composites. The epoxy clay nanocomposites have higher initial onset degradation temperatures ($T_{10\%}$) compared to those of neat epoxy as shown in Table 5.3. $T_{10\%}$ decreases with increase in clay loading. Such a degradation behaviour is probably associated with the morphological changes in relative proportion of exfoliated and intercalated species with the clay loading. Similar trend was also observed in the case of maximum degradation temperature ($T_{\text{max}}$). A maximum increase in residual weight at 700°C (63.1 %) was shown by epoxy/3 phr clay nanocomposite. Hence, it can be concluded that exfoliated clay nanocomposite can improve the thermal stability by increasing the initial stage of degradation, delaying the degradation temperature and forming reasonably high amount of char residue. The barrier effect of clay layers on the volatilization of degradation product is higher in system having high amount of clay loading (3 phr), where the intercalated structure is the dominant population and, even when char is formed in higher quantity.

Even though $T_{10\%}$ of CTBN is higher than epoxy, the epoxy/CTBN blend has a lower $T_{10\%}$ than the neat epoxy due to the reduction in crosslink density by the incorporation of phase separated CTBN particles. The thermal stability of the epoxy/CTBN/clay nanocomposite was found to depend on the dispersion of nanoclay rather than its localization in the blend component. An enhancement in $T_{10\%}$ and $T_{\text{max}}$ values are shown by epoxy/clay/CTBN nanocomposites with 1 and 2 phr clay loading when compared with
epoxy/clay nanocomposites having same amount of nanoclay. This may be due to the increased d spacing between the clay layers by the interpenetration of low molecular weight CTBN, as confirmed from XRD results. The effect of CTBN on cross-linking does not affect the thermal degradation performance of the epoxy/clay/CTBN nanocomposites.

5.3 Conclusion

The effect of clay loading on the morphology and hence the properties of epoxy/clay and epoxy/clay/CTBN nanocomposites were studied. The clay platelets were exfoliated and well dispersed in epoxy/clay and epoxy/clay/CTBN nanocomposites with 1 phr clay loading. An intercalated with occasional exfoliation was obtained for 2 and 3 phr clay loaded systems. The presence of tactoids in 3 phr clay loaded systems was detected. Due to the preferential interaction between organically modified clay and CTBN which was confirmed from series of experiments, the low molecular weight CTBN easily interpenetrated into the clay galleries causing further increase in the d spacing between the clay platelets in epoxy/clay/CTBN nanocomposites. Moreover, the presence of a significant portion of clay platelets inside the phase separated CTBN phase were noticed in epoxy/1 phr clay/15 phr CTBN nanocomposite. Highly delaminated clay platelets could easily get inside the CTBN phase and increase the CTBN domain size. The intercalated clay layers in 2 and 3 phr clay loaded epoxy/clay/CTBN nanocomposites located in the epoxy matrix, with a tendency to align near the phase separated CTBN. Clay platelets at the epoxy-CTBN interface suppress the coalescence of the rubber particles during phase separation and resulted in lower domain size of CTBN particles. The revealed morphology in epoxy/clay and epoxy/clay/CTBN nanocomposites was reflected in their viscoelastic and mechanical properties. Greatest reinforcing effect occurred above the glass
transition temperature in all the nanocomposites except epoxy/1 phr clay/15 phr CTBN system. In epoxy/1 phr clay/15 phr CTBN system, due to its morphological distinctiveness, the clay effectively reinforced only in ambient temperatures. While all the other clay filled samples presented here showed a higher Tg value than its unfilled variant, epoxy/1 phr clay/15 phr CTBN system showed a lower Tg value. The constrained epoxy volume in epoxy/1 phr clay/15 CTBN was lower than that of epoxy/1 phr clay nanocomposite due to lesser interaction of nanoclay and epoxy network as most of the delaminated individual clay platelets were inside the phase separated CTBN phase. However, the constrained epoxy volume in epoxy/clay/CTBN nanocomposite having higher amount of clay (2, 3 phr) was much higher than that in corresponding epoxy/clay binary nanocomposite due to the increased ‘d’ spacing between clay platelets by the penetration of CTBN into the clay galleries. The 1 phr clay loaded epoxy/clay nanocomposite and epoxy/clay/CTBN nanocomposites showed maximum flexural and tensile modulus values. The thermal degradation properties of epoxy/clay/CTBN nanocomposites depend on the dispersion of clay rather than its distribution among the blend component. Hence the trend in thermal degradation parameters was similar in epoxy/clay and epoxy/clay/CTBN nanocomposites. The exfoliated nanostructure both in epoxy/clay and epoxy/clay/CTBN nanocomposite with 1 phr clay loading favoured good thermal stability. An enhancement in thermal degradation parameters, showed by epoxy/clay/CTBN nanocomposites with 1 and 2 phr clay loading when compared with epoxy/clay nanocomposites having same amount of nanoclay, was due to the increased d spacing between the clay layers by the interpenetration of low molecular weight CTBN.
5.4 References


