CHAPTER 5

Hydroxyl terminated poly (ether ether ketone) with pendant methyl group toughened epoxy clay ternary nanocomposites having hydroxyl functionalized quaternary alkyl ammonium modified clay

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5.1 Introduction

The previous chapters, chapter 3 and chapter 4, described the effect of quaternary alkyl ammonium modified clay and primary alkyl ammonium modified clay respectively on the morphology and thermo mechanical properties of PEEKMOH toughened epoxy clay ternary nanocomposites. Due to higher bronsted acidity of the later produced an exfoliated structure as reported by Lan et al [1] and showed improved mechanical properties compared to former. Due to the thermal dissociation of primary alkyl ammonium modified clay at the cure temperature of epoxy amine reaction adversely affect the stoichiometry of epoxy amine ratio resulting in low $T_g$. Stoichiometry of the epoxy amine reaction needs to be adjusted as per the thermal dissociation kinetics of the primary alkyl ammonium modified clay in order to achieve high $T_g$ with the total consumption of hardener in the curing process. It is reported that quaternary alkyl ammonium surfactants containing hydroxyl groups also provide an exfoliated clay structure due to the high bronsted acidity [1].

Chapter-5 focuses on the effect of hydroxyl functionalisation of the clay modifier on the surface morphology and thermo mechanical properties of the PEEKMOH toughened epoxy clay ternary nanocomposites. The organoclay used for the present study is hydroxyl functionalised quaternary alkyl ammonium modified clay (Cloisite 30B).

5.2 Experimental

5.2.1 Materials

High purity methyl hydroquinone (MeHQ) (Aldrich), 4,4'-difluoro benzo phenone (DFBP) (Spectrochem, India), anhydrous potassium carbonate (BDH, India), N-methyl-2- pyrrolidone (NMP) (SRL, India), Toluene (Qualigens, India) were used for the synthesis of PEEKMOH. MeHQ and DFBP were vacuum dried at 70°C and 60°C respectively. Anhydrous potassium carbonate was dried at 400°C in a muffle furnace before use. NMP was distilled under reduced pressure over $P_2O_5$ and stored over molecular sieves. Toluene was distilled over sodium and stored over sodium wire. DGEBA epoxy resin (LY 556, Ciba Geigy) with an epoxide equivalent weight 188.68g/mol and high purity 4,4'-diamino diphenyl
sulphone (DDS) (Merck) were used as received. Tri phenyl phosphine (TPP) (Aldrich) was dried before use. Cloisite 30B (Southern clay product) [methyl tallow (bis-2-hydroxy ethyl) quaternary ammonium modified montmorillonite, 

\[d_{001}=1.83 \text{ nm, CEC } = 95 \text{ meq/100g clay, specific gravity } = 1.98\text{g/cc}\] was dried under vacuum at 70°C before use.

5.2.2 Synthesis of PEEKMOH Oligomer

Hydroxyl terminated PEEK oligomer having pendant methyl groups with number average molecular weight \((M_n) = 12,000 \text{ g/mol (Theoretical)}\) was synthesized by aromatic nucleophilic displacement of fluorine from an activated substrate, 4,4'-difluoro benzophenone (DFBP) by methyl hydroquinone (MeHQ) as discussed in Chapter 3.

5.2.3 Preparation of PEEKMOH toughened epoxy clay ternary nanocomposites

PEEKMOH toughened epoxy clay ternary nanocomposites were prepared as per the Scheme 3.2 given in chapter 3. For all compositions, PEEKMOH concentration was maintained at 5 phr.

5.2.4 Characterization

The nanocomposites were characterized by DSC, XRD, TEM, TMA, DMA, Tensile, flexural, Fracture toughness, SEM and TGA as per the details described in chapter-2.

5.3 Results and Discussion

5.3.1 Cure behavior

The cure morphology of the PEEKMOH toughened epoxy clay ternary nanocomposites was monitored by dynamic DSC. The onset of the exotherm and the maximum cure temperature showed an increase from 125 to 130°C and 221 to 225°C respectively by the incorporation of PEEKMOH into epoxy DDS system (Fig 5.1 a & b) while the incorporation of Cloisite 30B into PEEKMOH toughened epoxy system reduced the same to 121°C (Fig 5.1c) revealing the catalytic effect of clay particles on toughened epoxy DDS system. Similar observations have been made for Cloisite 25A system in Chapter 3. DSC curve of epoxy-Cloisite 30B mixture without the hardener shows an onset of exothermic peak at 260°C in
Fig 5.2 indicating the thermal dissociation of clay modifier does not happen at the cure temperature (200°C). Therefore, in Fig 5.1c, single stage cure reaction is observed as in the case of Cloisite 25A system.

![Fig 5.1 DSC scans of epoxy amine reaction a) epoxy-DDS b) epoxy-DDS-PEEKMOH and c) epoxy-DDS-PEEKMOH-Cloisite 30B](image)

![Fig 5.2 DSC Scan of epoxy with Cloisite 30B](image)
5.3.2 X-ray analysis

In Fig 5.3, curve (a) represents the wide angle XRD pattern of Cloisite 30B powder. It can be seen that the [001] diffraction peak of this organically modified clay appeared at $2\theta = 4.81^\circ$ with an interlamellar spacing ($d_{001}$) of $1.83$ nm as calculated from Bragg's law given in equation (1).

$$n \lambda = 2d \sin \theta \quad (1)$$

where $n$, an integer, $\lambda$, the wavelength, $\theta$, the glancing angle of incidence and $d$, the interplanar spacing of the clay layer.

Fig 5.3 X ray diffraction patterns of Cloisite 30B and its epoxy based ternary nanocomposite  (a: Cloisite 30B, b: Epoxy/3 phr Cloisite 30B, c: Epoxy/3 phr Cloisite 30B /5phr PEEKMOH)

Fig 5.3, curve (b) shows the XRD pattern of epoxy / 3 phr Cloisite 30B without thermoplastic modifier. The diffraction peak is shifted to $2\theta = 2.49^\circ$ and the d-spacing is increased to $3.54$nm, since the epoxy -hardener matrix is entered into the clay galleries. The diffractogram of Fig 3(c) represents the X-ray diffraction of nanocomposite with $5$phr PEEKMOH and $3$ phr Cloisite 30B where the diffraction peak is shifted to $2\theta = 2.35^\circ$ with an increase of d spacing to $3.75$nm. The increase in d spacing by the incorporation of PEEKMOH is not
substantial. This may be due to the fact that high molecular weight of PEEKMOH \( (M_n = 12000 \text{ g/mol}) \) is expected to diffuse less in between the clay layers compared to the low molecular weight constituents of epoxy \( (188 \text{ g/mol}) \) and DDS \( (248 \text{ g/mol}) \). Similar observations were made by Isik et al for epoxy resin–polyether polyol organically treated montmorillonite ternary nanocomposites [2].

### 5.3.3 Transmission Electron Microscopy (TEM)

TEM pictures of nanocomposite are shown in Fig 5.4. Epoxy/3 phr Cloisite 30B system (Fig 5.4a) shows an intercalated structure whereas Epoxy/3 phr Cloisite 30B / PEEKMOH (Fig 5.4b) system shows an intercalated morphology with more interlamellar spacing. For PEEKMOH toughened epoxy system, Clay distribution was found to be mostly in the epoxy phase with occasional distribution in thermoplastic phase. As reported in the literature (3-5), organically modified montmorillonite with functional hydroxyl group \( (C_{18} \text{ OH MMT}) \) could be completely exfoliated in DGEBA when DDS was used as curing agent. We failed to observe exfoliated structure and this may be due to increase in viscosity by the incorporation of PEEKMOH. Peng et al [6] have observed similar behavior for \( C_{18} \text{OH MMT} \) in the epoxy / poly ether imide (PEI) hybrid nanocomposite system developed by solution mixing technique where intercalated structure was accompanied by a partly exfoliated structure and they also explained that it is due to high molecular weight PEI. The strong interactions between epoxy molecules, PEEKMOH and the surface of silicate platelets through hydroxyl groups resulting from the chemical reaction and physical adhesion and the geometric confinement effect of the inorganic fillers to the mobility of molecules are crucial to increase the viscosity. Yasmin et al [7] have observed exfoliated structure with occasional presence of intercalates for 1wt% montmorillonite modified with methyl tallow (bis-2-hydroxy ethyl) quaternary ammonium salt/epoxy system using methyl tetrahydro phthalic anhydride as hardener and three roll mill as a clay dispersion device. Miyagawa et al [8] have observed intercalated morphology for montmorillonite modified with methyl tallow (bis-2-hydroxy ethyl) quaternary ammonium salt/epoxy system using triethylene tetramine as hardener and sonication technique for dispersion in solvent medium. In the present...
system, we failed to observe exfoliation for Cloisite 30B /epoxy –DDS and this may be due to the fact that ultrasonication technique for clay dispersion may not be good enough to allow the entry of high viscous mass of epoxy –DDS mixture into the clay galleries. We believe that high shear mixing technique for clay dispersion may yield exfoliated structure for high viscous resin system as it is observed by Zunjarrao et al for diglycidyl ether of bisphenol F (DGEBF) epoxy resin with aliphatic amine curing agent [9].

![Fig 5.4 TEM of a) Epoxy/3 phr Cloisite 30B and b) Epoxy/3 phr Cloisite 30B / PEEKMOH ternary nanocomposite](image)

5.3.4 Izod impact strength

Izod impact strength and impact energy values of epoxy clay ternary nanocomposites are given in Table 5.1. The data reveals that the strength and energy were radically decreased to 50-55% with 3 phr clay loading thereafter it remains stable. It is noticed from Table 5.2 that as the clay concentration increases from 1 phr to 8 phr the percentage strain (plastic behavior) decreases and this suggests that the nanocomposites were more rigid than the neat epoxy. As a result, the Izod impact strength and impact energy were decreased with the addition of clay nanoplatelets. Addition of PEEKMOH in to epoxy-clay nanocomposites could not improve the impact strength and impact energy to great extent. Similar results
were reported for anhydride cured epoxy clay nanocomposites [10] and amine cured epoxy clay nanocomposite [8]. It has also been reported that the addition of silica nanoparticles results in the improvement of the Izod impact strength of both amine and anhydride cured epoxies [11]. Therefore, it can be concluded that clay nanoplatelets are not suitable for improving the Izod impact strength and energy even in the presence of thermoplastics (PEEKMOH) although they do improve the modulus because of the large aspect ratio of nanoclay platelets.

**Table 5.1** Izod impact energy and strength, CTE and \( T_g \) of the epoxy clay ternary nanocomposites \( (T_g \text{ by DMTA (from } \tan \delta)) \)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Impact Energy ((J))</th>
<th>Impact Strength ((Jm^{-1}))</th>
<th>CTE ((\mu m/\circ C)) Below ( T_g )</th>
<th>( T_g ) ((^\circ C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>0.146±0.013</td>
<td>37±3</td>
<td>96</td>
<td>223</td>
</tr>
<tr>
<td>Epoxy/PEEKMOH</td>
<td>0.154±0.006</td>
<td>38±2</td>
<td>91</td>
<td>218</td>
</tr>
<tr>
<td>Epoxy/ Cloisite 30B (1phr) /PEEKMOH</td>
<td>0.085±0.021</td>
<td>20±5</td>
<td>70</td>
<td>216</td>
</tr>
<tr>
<td>Epoxy/ Cloisite 30B (3phr) /PEEKMOH</td>
<td>0.072±0.007</td>
<td>17±1</td>
<td>86</td>
<td>210</td>
</tr>
<tr>
<td>Epoxy/ Cloisite 30B (5phr) /PEEKMOH</td>
<td>0.068±0.003</td>
<td>17±2</td>
<td>86</td>
<td>209</td>
</tr>
</tbody>
</table>

### 5.3.5 Thermo Mechanical Analysis

Coefficient of thermal expansion (CTE) of the ternary nanocomposites is given in Table 5.1. The data reveals that CTE values decreases with the addition of PEEKMOH to the epoxy system and it further decreases with the addition of clay. This is because of the mobility of the epoxy chains restricted by the addition of thermoplastic as well as the rigid clay particles with large surface area. The decrease in CTE may also be due to the uniform and nanolevel distribution of clay particles in epoxy matrix and also due to efficient stress transfer to clay layers. The reduction in CTE with the incorporation of clay platelets was also reported by several authors [7, 12]. The decrease in CTE was prominent for 1 phr clay addition to the PEEKMOH toughened epoxy system thereafter CTE increases steadily with
clay concentration. This may be due to the agglomeration of clay platelets, which will decrease the surface area and stress transfer efficiency of clay platelets.

5.3.6 Dynamic Mechanical Analysis

Fig 5.5 Storage modulus Vs temperature of epoxy clay ternary nanocomposite

Fig 5.6 Tan Delta Vs temperature of epoxy clay ternary nanocomposite
Fig 5.7 Loss modulus Vs Temperature of epoxy clay ternary nanocomposites

The storage modulus (E') and tan δ values of the neat epoxy and the epoxy clay ternary nanocomposites are plotted against temperature in Fig 5.5&5.6 respectively. In accordance with the results of the tensile and flexural tests, the E' of the epoxy clay ternary nanocomposites increase with the clay concentration below T_g. The increase in E' is found to be around 100% at 50°C to 100°C compared to neat epoxy resin upto 3 phr Cloisite 30B addition there after it levels off. In the present system the improvement in E' is found to be 37% higher at every temperature for 3 phr clay addition compared to montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium salt filled system as reported in Chapter 3. This may be due to the fact that the functional OH groups of Cloisite 30B had better interaction with epoxy as well as with PEEKMOH compared to the non functional montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium salt. As the temperature increases, nanocomposites show a gradual drop in storage modulus upto the glass transition temperature. In the rubbery region, the storage modulus is decreased marginally for PEEKMOH toughened epoxy system due to softening of PEEKMOH above T_g. But the addition of clay into the PEEKMOH toughened
The dynamic mechanical spectrum of the nanocomposites show only a single $T_g$ (Fig 5.6). Though two $T_g$'s, corresponding to epoxy rich and thermoplastic rich phases are expected as it is observed in PEEKMOH toughened epoxy system [13], only one $T_g$ is observed because of the low molecular mass of PEEKMOH and also due to the suppression of the mobility of thermoplastic fragments by rigid nanoclay layers. The $T_g$ of the epoxy rich phase decrease with the addition of PEEKMOH. This is due to the presence of a small amount of PEEKMOH remaining in the epoxy matrix. The decrease may be due to the decrease in cross link density of the blends as a result of the reaction between epoxy and hydroxyl group of PEEKMOH. It is also noticed that $T_g$ is further decreasing with increase in clay content in ternary nanocomposites as shown in Table 1. This may be due to the plasticizing effect of organic modifier of clay layers. A lower $T_g$ with higher clay content is also reported by many other authors [14-18].

Yasmin et al [7] have suggested that the interaction of the polymer chain with the high specific surface area of clay particles can drastically alter the chain kinetics in the regions surrounding them and lead to a lower cross-link density. Another possible reason for the decrease in $T_g$ could be the formation of matrix interface between the silicate layers [18,19] where properties are different than that from the bulk of the matrix. It can also be due to plasticization of epoxy by surfactants (organic modifier) chains present on the clay layers as suggested by Chen et al [18].

Interestingly, loss modulus ($E''$) against temperature plot for nanocomposites reveal two peaks (Fig 5.7). The peak between 130 and 160°C corresponds to the $T_g$ of PEEKMOH rich phase and the peak at higher temperature corresponds to epoxy rich phase. The lowering of $T_g$ is also observed in the loss modulus curve of nanocomposites with increase in clay content. Loss modulus ($E''$) is also found to be higher for the nanocomposites below and above glass transition temperature compared to neat resin system.
### 5.3.7 Tensile and Flexural Properties

Table 5.2 Fracture toughness, Tensile and Flexural properties of epoxy clay ternary nanocomposites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tensile Modulus (G Pa)</th>
<th>Tensile Strength (M Pa)</th>
<th>Flexural Modulus (G Pa)</th>
<th>Flexural Strength (M Pa)</th>
<th>Percentage Strain</th>
<th>Fracture toughness (M Pa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>1.53±0.02</td>
<td>63±4</td>
<td>2.95±0.11</td>
<td>122±6</td>
<td>3.4±0.3</td>
<td>1.16±0.16</td>
</tr>
<tr>
<td>Epoxy/PEEKMOH</td>
<td>1.44±0.04</td>
<td>72±6</td>
<td>2.86±0.12</td>
<td>112±6</td>
<td>9.3±0.2</td>
<td>2.17±0.19</td>
</tr>
<tr>
<td>Epoxy/PEEKMOH/Clayite 30B (1phr)</td>
<td>1.58±0.02</td>
<td>65±4</td>
<td>3.24±0.05</td>
<td>112±10</td>
<td>6.3±0.2</td>
<td>1.92±0.17</td>
</tr>
<tr>
<td>Epoxy/PEEKMOH/Clayite 30B (3phr)</td>
<td>1.59±0.06</td>
<td>64±4</td>
<td>3.28±0.02</td>
<td>110±11</td>
<td>5.6±0.3</td>
<td>1.74±0.06</td>
</tr>
<tr>
<td>Cloisite 30B (5phr)</td>
<td>1.60±0.04</td>
<td>59±7</td>
<td>3.42±0.05</td>
<td>113±9</td>
<td>4.8±0.1</td>
<td>1.56±0.18</td>
</tr>
<tr>
<td>Epoxy/PEEKMOH/Clayite 30B (8phr)</td>
<td>1.71±0.06</td>
<td>56±6</td>
<td>3.58±0.08</td>
<td>98±4</td>
<td>4.2±0.2</td>
<td>1.46±0.11</td>
</tr>
</tbody>
</table>

Tensile and Flexural properties of ternary nanocomposites are given in Table 5.2. The perusals data reveals that tensile strength of PEEKMOH toughened epoxy system was found to be higher than the neat epoxy system and this may be due to the fact that the PEEKMOH domains may act as crack stoppers and increases the tensile strength. But the tensile strength is decreasing with increase in clay content at constant PEEKMOH content (5 phr). This is attributed to higher stress concentration effect of clay agglomerates at higher clay contents. Non exfoliated clay particles form larger agglomerates, and thus clay polymer surface interaction decreases as the clay content increases resulting in lower tensile strength as it was observed elsewhere [2]. Another reason is that as clay content increases, the viscosity of the system increases resulting in heterogeneity and nanovoids formation due to the entrapment of air bubbles during sample preparation [14, 20-22]. Similar observations are noticed in polyether polyl modified epoxy montmorillonite ternary nanocomposites [2] and other epoxy montmorillonite nanocomposites [23, 24]. But there is a marginal improvement in tensile strength for the present system compared to montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium salt system.
reported in Chapter 3, due to the presence of functional hydroxyl groups in Cloisite 30B which enhances the interfacial interaction between clay layers and polymer matrix. It is important to note that the low tensile strength observed here can be improved by better processing techniques as discussed earlier [25].

The tensile moduli and flexural moduli of ternary nanocomposites are found to be increased to great extent with the increase in Cloisite 30B concentration. An increase of 12% and 19% tensile moduli was observed for PEEKMOH toughened epoxy clay ternary nanocomposites with respect to neat epoxy and PEEKMOH toughened epoxy system respectively with the 8 phr Cloisite 30B incorporation. Qi et al [26] have observed 15.1% improvement in tensile moduli by the addition of 10% montmorillonite modified with methyl tallow (bis-2-hydroxy ethyl) quaternary ammonium salt to DGEBA epoxy system. Similarly it is also found 17.2% enhancement in tensile modulus for 7wt % montmorillonite modified with methyl tallow (bis-2-hydroxy ethyl) quaternary ammonium salt to the epoxy system by Basara et al [24]. In general, the tensile modulus increases with increasing amount of montmorillonite at constant thermoplastic content. The modulus of a composite depends on the ratio of filler modulus to matrix material modulus [27]. Since montmorillonite has a higher modulus than the polymeric matrix, the modulus increases with the clay content. In the present system, flexural moduli was increased significantly to 22% and 25% for 8phr Cloisite 30B incorporation with respect to epoxy and PEEKMOH toughened epoxy matrix respectively compared to the increase of 10 and 14% for 8phr montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium salt incorporation (Cloisite 25A) as reported in Chapter 3. The increase in modulus may be explained in terms of strong interfacial interactions between polymer matrix and functional hydroxyl groups of rigid silicate layers and also due to better dispersion of Cloisite 30B in epoxy matrix.

5.3.8 Fracture toughness

The fracture toughness values of the nanocomposites are given in Table 5.2, which are expressed in stress intensity factor (KIC). The fracture toughness of the neat epoxy system was increased to 87% by the addition of PEEKMOH
PEEKMHOH...hydroxyl functionalized quaternary alkyl ammonium modified clay Chapter 5

oligomer. This may be due to two-phase morphology of the blends and chemical interaction between the hydroxyl groups of thermoplastic and epoxy. The fracture toughness of the neat epoxy system was increased to 66% by the addition of 1 phr Cloisite 30B to the PEEKMOH toughened epoxy system which is 21 % higher than the Cloisite 25A as reported in Chapter 3. The fracture toughness value was found to be higher for Cloisite 30B system compared to montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium salt (Cloisite 25A) for all compositions of clay loading up to 8 phr. This may be due to hydrogen bonding or polar interactions between functional hydroxyl groups of organically modified Cloisite 30B and PEEKMOH and epoxy resin. The enhancement in toughness of nanocomposites over neat epoxy can be attributed to the well dispersion of clay particles, efficient stress transfer through clay layer as well as increase in interfacial interaction between clay particles and epoxy. It has been reported that the increase in fracture surface area due to the crack path deflection is the major toughening mechanism in the epoxy-clay nanocomposites [23]. Recently Zunjarrao et al [9] reported that fracture toughness of epoxy clay system was increased to 35% and 20% with 2% volume fraction of montmorillonite modified with octadecyl ammonium salt incorporation by shear mixing and ultrasonication respectively. Qi et al [26] have reported 25% improvement in fracture toughness with 5% montmorillonite modified with methyl tallow (bis-2- hydroxy ethyl) quaternary ammonium salt incorporation in epoxy clay nanocomposites. Zilg et al [14] have suggested that the exfoliated structure mainly leads to an improved modulus while the intercalated clay platelets lead to an improved toughness. In the present system, X- ray and TEM pictures of nanocomposites with and with out thermoplastic showed an intercalated morphology confirming that both thermoplastic and Cloisite 30B are contributing increase in toughness. This is further supported by the % strain at break values of ternary nanocomposites as shown in Table 5.2. However, as the clay content increases, percentage strain at break and fracture toughness decreases steadily for ternary nanocomposites revealing that thermoplastic is the main contributing factor for the increase in percentage strain at break and toughness of the nanocomposites
rather than the clay alone. At higher clay concentration, there is a possibility of the isolated agglomeration of clay particles. These isolated clay particle agglomerates can act as failure sites from where the crack initiates and thus reduce the stress intensity factor.

5.3.9 Scanning Electron Microscope (SEM)

The phase morphology of the PEEKMOH toughened epoxy system and the clay filled PEEKMOH toughened epoxy ternary nanocomposites is studied using scanning electron microscopy. The scanning electron micrographs of cryogenically fractured surfaces of epoxy/PEEKMOH and epoxy /PEEKMOH/3 phr Cloisite 30B are shown in Fig 5.8 a &b respectively. The cryogenically fractured surfaces are etched with chloroform to get a clear picture of the morphology. Two phase morphology is clearly evident from the micrograph. No phase inversion or continuous morphology is observed. The phase separation is occurred by nucleation and growth mechanism due to off critical composition of the thermoplastic in liquid epoxy as calculated by Flory –Huggins model [28]. Here gelation followed by vitrification occurred after the phase separation. It is found that the domain size of PEEKMOH and distance between the domains decreases with the addition of clay. The domain size of the thermoplastic depends on the viscosity and the rate of curing of epoxy matrix. It is reported that the bronsted acidic nature of the organic moiety present in the clay enhances the rate of curing reaction resulting to high viscous system. In highly viscous systems gelation could occur at an early stage giving rise to smaller domains. After the initial formation of the domains coalescence of the separated domains takes place if the viscosity is low enough and results in large domains. In highly viscous system, the extent of coalescence was less and as a result the domain size will be small and it is further confirmed from SEM of tensile failed specimen (Fig 5.9 b). On the contrary, Isik et al [2] have reported the increase in domain size by the incorporation of clay into the polyether polyol toughened epoxy system. This may be due to the low molecular mass of polyether polyol used resulting in low viscous system.

The scanning electron micrograph of the tensile failed specimens of epoxy and epoxy /PEEKMOH/5 phr Cloisite 30B are shown in Fig 5.9 a&b respectively.
The failed surface of neat epoxy resin show typical characteristic of brittle fracture. The surface is smooth and the crack propagation is uninterrupted. The failure surface of epoxy/ PEEKMOH /5 phr Cloisite 30B is rough with ridge patterns and river markings could also be seen on the fracture surface. The roughness of the fracture surface is due to two reasons. First it is an indication of crack path deflection. Second the roughness indicates the ductile nature of the crack. The matrix becomes less brittle in comparison with the unmodified epoxy because of a decrease in the cross-link density. The polar hydroxyl groups of PEEKMOH enhance the interfacial adhesion either through the opening of epoxy ring or through the hydrogen bonding interactions between the matrix and oligomer. Similarly strong interfacial/polar interactions between the functional OH groups of organic moiety of clay and epoxy and PEEKMOH of ternary nanocomposites influenced the crack path deflection. Another factor responsible for the increase in the fracture toughness was the local plastic deformation of the matrix. The dispersed domains acted as stress concentrators, and this lead to the plastic deformation of the matrix surrounding the domains. According to Hedrick et al [29] river markings on the fracture surface are an indication of plastic deformation of the matrix. On careful observation of Fig 5.9 b, it reveals that crack path deflection sites are found to be more with thermoplastic inclusion.

Fig 5.8 SEM images of cryogenically fractured surfaces of a) epoxy/PEEKMOH b) epoxy/3 phr Cloisite 30B / PEEKMOH
Scanning electron micrograph of the fracture toughness failed surface of epoxy, epoxy/PEEKMOH, epoxy/3phr Cloisite 30B and epoxy/PEEKMOH/3phr Cloisite 30B are given in Fig 5.10 a-d. The fracture surface of neat epoxy system exhibits an uninterrupted and featureless crack propagation resulted from the brittle failure of epoxy. In contrast fracture surface of 5 phr PEEKMOH toughened epoxy (Fig 5.10b) show an improved toughness characterized by crack path deflection, rough and ridge patterns with river marking lines. Since the samples are etched with CHCl₃, the domains of PEEKMOH are visible. It is clear that most of the cracks were interrupted and deviated in front of the PEEKMOH domains. Hence the great increase in toughness of PEEKMOH toughened epoxy is due to the action of phase separated thermoplastic as crack arresting points. The fracture surface of 3 phr clay incorporated epoxy (Fig 5.10 c) show only slight improvement in toughness as evidenced from the agglomerated and debonded clay particles around the onset of crack deflection. Liu et al [30] have also observed similar fractographic appearance for nanoclay filled epoxy systems. Fig 5.10d shows the typical fracture surface of 3 phr clay and 5 phr PEEKMOH reinforced epoxy ternary nanocomposites. The micrograph shows a better dispersion of clay particles as well as presence of PEEKMOH in the ternary nanocomposites with rough fracture surface and crack path deflection. The fracture toughness of the PEEKMOH toughened epoxy clay system is improved compared to epoxy clay nanocomposites, but inferior to PEEKMOH toughened epoxy blend. This positive and negative effect can be attributed to two phase morphology with PEEKMOH
and the pull out of clay particles during fracture respectively. However, the addition of clay particles to the PEEKMOH toughened epoxy blend reduces the toughness, but increases the modulus.

Fig 5.10 SEM images of fracture toughness failed surfaces of a) epoxy b) epoxy/PEEKMOH c) epoxy/3 phr Cloisite 30B and d) epoxy/PEEKMOH/3 phr Cloisite 30B

5.3.10 Thermo gravimetric Analysis

The thermal stability of the PEEKMOH toughened epoxy clay ternary nanocomposites is studied by thermo gravimetric analysis and the thermograms are given in Fig 5.11. From the figure it reveals that the degradation started at 340°C for epoxy DDS system while it was at 324°C for PEEKMOH toughened epoxy DDS system which may be due to decrease in cross link density. But with incorporation of clay the thermal stability of PEEKMOH toughened epoxy DDS system increases as evidenced from the increase in onset of thermal degradation temperature with increase in clay content. This enhanced thermal stability may be ascribed due to the action of silicate layers as an effective barrier to the volatile products generated during decomposition and char formation.
5.4 Conclusions

PEEKMOH toughened epoxy clay ternary nanocomposites were processed by melt mixing of PEEKMOH with epoxy along with clay by mechanical stirring followed by ultrasonication. Intercalated morphology of nanoclay platelets in the nanocomposites has been clearly identified from TEM and small angle X-ray diffraction. The increase in tensile moduli, flexural moduli and fracture toughness is found to be much higher for Cloisite 30B based nanocomposites compared to Cloisite 25A counterparts reported in Chapter 3 with respect to neat epoxy system. Similarly, percentage strain is also higher for nanocomposites. Izod impact strength and impact energy decrease considerably with the incorporation of clay.

Storage modulus and loss modulus are higher for the nanocomposites below and above glass transition temperature compared to neat resin system. The increase is much higher in the present system compared to Cloisite 25 A based ternary nanocomposites reported in Chapter 3 due to better interaction between the phases through polar hydroxyl groups of the Cloisite 30B. The lowering of $T_g$ is observed with increase in clay content in the Dynamic Mechanical Analysis of the
blends. The CTE values are decreasing up to 1 phr clay incorporation thereafter it increases.

Scanning electron microscopy reveals that phase separation occurs by nucleation and growth mechanism. The viscosity of the system increases with the addition of clay during the cure reaction leading to gelation at an early stage resulting in decrease of PEEKMOH domain size. The area of crack path deflection and river markings are increased with nanoclay incorporation confirming that nanoclay is not only taking part in improving the stiffness, but also in toughness of the nanocomposites along with thermoplastic. The onset of thermal degradation is improved with increase in clay content.

5.5 References