In this chapter, the preparation of epoxy – high density polyethylene fabric – clay composite laminates and their mechanical, thermal, flame retardant, morphological properties will be discussed.

5.1 Introduction

Polymer composites and their laminates are integral components of modern society. Polymer laminates have been used in various fields. Polymer laminate materials are prepared from thin sheets or fabrics of polymer and other materials that are commercially available by stacking them to form a single component. These layers are bonded together using thermal and pressure sensitive adhesives such as epoxy, polyesters, etc. These kinds of materials are being used in fields such as waste containment facilities, flooring, agriculture sector, roofing, packaging, etc [Timothy D Stark, 1996]. In the form of flexible films and laminates for bags and as semi-rigid and rigid containers as well as in pipe extrusion and injection Molding of different items widely used polymers are low density polyethylene (LDPE), medium density polyethylene (MDPE) and high density polyethylene (HDPE) [D M Price et al, 1999]. Some of the other examples include carbon fabric reinforced polymeric composites and laminates in components such as flaps, landing-gear doors, and other artifacts used in aeronautical industry. These composite laminates are also being used in sports utilities such as aileron, head guard, etc. Other areas like home construction, navy, and automotive industries utilizes the benefits of lightweight and high strength laminate materials [Jane Maria Faulstich de Paivaa et al, 2006]. HDPE film is a good
candidate as the liner material since it possesses good strength, outstanding chemical resistance and minimal extractable matter, which might permeate and contaminate the water [John W Connell, 2003]. To improve the performance of the existing laminates further addition of reinforcements has been reported. Polypropylene and modified polypropylene fibers have been used along with carbon fibers which resulted in improvement in impact resistance and thermal stability [RCL Dutra et al, 2000]. The laminates of flax fiber in recycled HDPE matrix have shown improvement in fracture toughness up to 20\% fiber fraction [A.C.N. Singleton et al, 2003]. The performance of composites or laminates during utilization is related to their mechanical properties, thermal resistance and thermal stability as a result of the suitable combination of reinforcement, polymeric matrix and processing technique [Schwartz MM, 1997; Pilato LA and Michno MJ, 1994]. Hybrid composites such as Nylon – 6,6, nanofabric interleaving in epoxy/carbon fiber have shown improved impact resistance by 60\% [Paul Akangah et al 2010]. Epoxy – nylon laminates when loaded with low quantity of clay have showed improved mechanical properties [T. Niranjana Prabhu et al, 2013]. Thermoset polymer epoxy resin possess better mechanical strength, chemical resistance and service temperature requirements, among the polymeric matrices, hence been used to maximum extent in many industries [Penn L S and Wang H, 1998; Shim SB et al, 1997]. Epoxy resin offers modifications in its chemical structure depending on the required application. Improvement in thermal, mechanical properties and flame retardancy is important for the materials application in different fields. Large numbers of polymers are used in domestic applications. To make them safer, there is a need to reduce their potential for ignition or burn. There are some
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chemical additives known as flame retardants that are being used to delay the ignition and control burn. Traditionally a number of halogen-based as well as phosphorous and some other compounds have the flame retardancy effect in polymers without reducing their other properties and quality. Since the halogenated compounds contaminate environment, halogen-free flame retardants have occupied the market [Kiliaris P and Papaspyrides C D, 2010; Levchik SV, 2007]. Some of inorganic flame retardants required to be reinforced at high volume loading which impacts negatively on the costs, process ability and quality of the product [Zhao C et al, 2005; Laoutid F et al, 2009]. The effect of clay particles reinforcement in low quantity on impact resistance, tensile and flexural strength, thermal stability and flame retardancy of Epoxy-HDPE laminates have been studied in the present work.

5.2 Experimental:

5.2.1 Materials

Huntsman Araldite MY740 Epoxy Resin (density 1.16 g/cm$^3$), K112 Accelerator and Aradur HY918 Hardener (a low viscosity anhydride hardener, density 1.2 g/cm$^3$) from Huntsman Advanced Materials (India) Private Limited, INDIA. HDPE interwoven fabric was obtained from Reliance Industries Limited, INDIA. The fabric had following morphological features: fibers in the fabric were of 115 μm dia, 2500 mesh count openings per square inch, 245 μm fabric thickness and 50 g/m$^2$. Cloisite-30B clay was procured from Southern Clay products Inc., USA. The average particle size as given by the supplier was 10μm with a density 1.98 g/ cm$^3$. All the chemicals were used without any modifications.
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5.2.2 Preparation of Composite Laminates

Laminate hybrids of epoxy – HDPE fabric (5 layers) were prepared by incorporating clay particles as reinforcement with a loading of 0.1 phr to 0.7 phr using conventional hand layup technique. Initially clay was mixed with 100 phr epoxy and stirred for 30 minutes at 1350 rpm using a conventional variable speed TANCO stirrer (PLT-184). Then 2 phr accelerator and 85 phr hardener were mixed with epoxy – clay mixture for another 5 minutes at 1350 rpm. The HDPE interwoven fabrics of the size 200mm x 100mm were dipped into the clay mixed epoxy and layered (5 layers) between two Teflon release sheets and rolled. The samples were cured at 100°C for 2 hour and post cured at 120°C for 4 hours between two iron plates.

5.2.3 Characterization Techniques

Izod Impact test (ASTM D256) was conducted using Tinius Olsen IT504 Impact Tester. UTM, Hounsfield, H50km, UK, was used for tensile testing (ASTM D638) and Flexural testing (ASTM D 790). Tensile testing was done with a stress range 3000MPa, strain range 300% and speed 5 mm/min, whereas flexural testing was performed in 3 point configuration.

Thermo-gravimetric analysis (TGA) was carried out using a TG/DTA 6300 SII Nano Technology Inc., Japan, in the temperature range between 30 and 650 °C at a heating rate of 10°C per min in nitrogen atmosphere with a flow rate of 60 ml/min. To check the flame retardant properties Underwriters Laboratories – 94 tests were conducted as per the procedure of Underwriters Laboratories, USA.
Morphology of impact broken samples was investigated using Environmental Scanning Electron Microscope, ESEM, Quanto – 200, FEI, Netherland.

5.3 Results and Discussions

5.3.1 Mechanical Properties

Neat epoxy – HDPE fabric laminates have showed the impact strength of $45 \pm 1.22$ J/m. When these laminates were incorporated with lower load of clay particles, have showed improvement in impact strength. 0.1 phr clay introduction into these laminates resulted in increase of impact strength to $55 \pm 1.47$ J/m. When clay composition was increased to 0.2 phr, impact strength was increased to $65.8 \pm 1.52$ J/m (Figure 5.1). However further increase in clay content into the laminates have resulted in decrease of impact strength, with 0.7 phr clay incorporation into the epoxy – HDPE fabric laminates have resulted in impact strength of $29.7 \pm 1.31$ J/m.

Tensile strength and Young’s modulus for the samples have shown the similar trend with epoxy – HDPE fabric laminate showing $15.00 \pm 0.72$ MPa and $450 \pm 18$ MPa respectively and 0.2 phr clay reinforced laminate sample showing the maximum values $21.32 \pm 0.57$ MPa and $640 \pm 24$ MPa respectively. Figures 5.2 and 5.3 depicts the tensile strength and Young’s modulus values respectively for all composite laminates. The tensile strength and Young’s modulus for 0.2 phr clay reinforced epoxy – HDPE fabric composite laminate is increased by nearly 42 % when compared to the neat laminate sample. Also the flexural strength for 0.2 phr clay reinforced epoxy – HDPE fabric composite laminate showed greater improvement ($54.10 \pm 2.3$ MPa) compared to the neat epoxy-HDPE sample ($29.23 \pm 1.2$ MPa) (Figure 5.4).
An increase in impact resistance is observed with the increase in clay loading to an extent; however it is decreased from 0.3 phr clay load onwards. This may be due to better dispersion of clay particles at lower clay loading, which might have contributed in the increased energy consumption to crack growth due to crack twisting as well as deflection [Zhao C et al, 2005]. The smaller particles at lower clay load, being more finely dispersed throughout the matrix, would provide a more effective crack trapping network in the matrix. At higher clay loading clay particles tend to agglomerate and act as stress concentrators and eventually decrease the impact strength [Laoutid F et al, 2009; T Ozava et al, 1996].

The increase in tensile strength, flexural strength and Young’s modulus in the composite laminates at lower clay loading could be attributed to the improved bonding strength due to the addition of organoclays [A Yasmin et al, 2006]. On the other hand, decrease in trend at higher loading is probably due to the formation of agglomerates or tactoids content cannot act efficiently in dissipating mechanical energy but instead have served as flaws or defects and crack initiation sites decreasing the tensile strength, flexural strength and Young’s modulus [T Ozava et al, 1996].

The percentage elongation has shown marginal increase from 2.1 ± 0.11 % for neat sample to a maximum of 2.4 ± 0.12 % (for 0.2 phr clay reinforcement), later which is decreased marginally with the increased clay loading (Figure 5.5). This may be due to the rigidity of clay structures which might have limited the plastic deformation of the polymer matrix [Ling Chen et al, 2003].
Figure 5.1 Impact Strengths of Epoxy – HDPE Fabric – Clay Composite Laminates.

Figure 5.2 Tensile Strengths of Epoxy- HDPE Fabric - Clay Composite Laminates.
Figure 5.3 Young’s Moduli of Epoxy-HDPE Fabric-Clay Composite Laminates.

Figure 5.4 Flexural Strength of Epoxy-HDPE Fabric-Clay Composite Laminates.
Figure 5.5 Percentage Elongation at break of Epoxy-HDPE Fabric - Clay Composite Laminates.

5.3.2 Thermal Properties

TGA is carried out at a given constant heating rate to find the thermal stability, thermal resistance and degradation kinetics of various insulating materials. The Initial degradation temperature (IDT) sometimes used to understand thermal stability of materials is taken at which weight loss reaches 5% [T Ozava et al 1996]. Temperature at maximum rate of degradation (T_{max}), Maximum rate of % weight loss, R_{max}, Temperature at 10% weight loss (T_{10}) and activation energies of epoxy-HDPE and the composite laminates are given in Table 5.1. It is observed that the introduction of clay particles into epoxy – HDPE fabric laminates resulted in increase of thermal resistance to an extent of clay loading (Fig 5.6). This may be due to the good adhesion
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between clay and epoxy, hindering the heat propagation thereby reducing degradation rate [A Yasmin et al, 2006].

![Thermograms of Epoxy-HDPE and Epoxy-HDPE-Clay Composite Laminates.](image)

Figure 5.6  Thermograms of Epoxy-HDPE and Epoxy-HDPE-Clay Composite Laminates.

The Horowitz–Metzger integral kinetic method [Horowitz HH and Metzger G, 1963] and Freeman and Carroll [Freeman ES and Carroll B, 1958] were applied to calculate the kinetic parameters. These methods determine the decomposition activation energy with only one heating rate. In this study, the TGA curves at a heating rate of 10°C/min. were used to calculate the degradation kinetics for all samples. Following is the equation derived by Horowitz–Metzger that is used to calculate the activation energy:

\[
\ln \left( \ln \left( \frac{1}{1 - \alpha} \right) \right) = \frac{E}{RT^2} \quad -----(1)
\]
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Where $E_a$ = energy of activation, $\theta = T - T_e$, $T =$ temperature at time $t$, $T_e =$ temperature at $W/W_0 = 1/e$, $(1/e = 0.368)$, $W_0 =$ Initial weight, $W =$ Weight at time $t$, ‘R’ is universal gas constant, 8.314 kJ/mol/K, and ‘$\alpha$’ is the heating rate.

Thus, a plot of $\ln \left( \ln \left( \frac{1}{1-\alpha} \right) \right)$ against $\theta$ should give a straight line whose slope gives $E_a$ (Fig 5.7).

The straight-line equation derived by Freeman and Caroll is in the form of

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_t} = n - \frac{E_a}{2.303R} \frac{\Delta(1/T)}{\Delta \log W_t}$$

(2)

Where $\frac{dw}{dt} =$ rate of change of weight with time, $W_t =$ weight loss at the completion of reaction - total weight loss up to time $t$ or weight of reactive constituent remaining in the sample, $E_a =$ energy of activation, $n =$ order of reaction, $T =$ Temperature. The plot between the terms $\frac{\log (dw/dt)}{\log W_t}$ vs $\frac{1/T}{\log W_t}$ gives a straight line and slope of which gives the energy of activation ($E_a$) and intercept on Y-axis as order of reaction (n) (Figure 5.8).

For both kinetic methods, the calculations have been done in the temperature range of 350°C - 410°C where major degradation has occurred linearly.

Thermal resistance (IDT) has shown an increase for the samples reinforced with clay platelets. To compare the degradation behaviors, Table 5.1 lists the derivative peak rate of decomposition of the samples along with other thermal degradation properties. The initial degradation temperature which is generally considered to understand the
thermal stability of a material [T Ozava et al, 1996] has shown improvement with the increase in clay content. High heat energy is required for laminate hybrids to attain the same percentage weight loss than that required for neat epoxy-HDPE laminates. Also $T_{10}$ (Temperature at 10 % weight loss) results have shown trends similar to that of IDT. Activation energy values evaluated by Horowitz – Metzger method range from 30.765 kJ/mol to 20.877 kJ/mol and that by Freeman-Caroll method are ranging from 29.230 kJ/mol to 24.391 kJ/mol.

The maximum rate of degradation, $R_{\text{max}}$ is another parameter used to understand the effect of filler on degradation behavior of a polymer [T. Niranjana Prabhu et al, 2007]. With the increase in clay content, the maximum rate of degradation $R_{\text{max}}$ has decreased and the activation energy ($E_a$) for laminate hybrids are marginally less than that of neat sample. Also the $R_{\text{max}}$ values for higher order clay addition have increased. As the temperature is increased the oxides of clay formed might accelerate the degradation. The improved thermal resistance at low clay composition (0.2 phr) may be attributed to its good dispersion and better barrier effect in the system.

However the thermal stability is decreasing when clay is added which is indicated by the decrease in $E_a$. Also there have been inconsistent results with respect to $E_a$ values. This is possibly because of the release of the low-molecular-weight surface modifiers used in Cloisite-30B with which the clay was treated to become an organo modified clay.
Figure 5.7 Horowitz-Metzger Kinetic Plot to find activation energy.

Figure 5.8 Freeman – Caroll Kinetic Plot to find activation energy.
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### Table 5.1 Thermal Properties of Epoxy-HDPE-Clay Composite Laminates

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT at 5% weight loss, °C</th>
<th>Temperature at 10% weight loss, $T_{10}$, °C</th>
<th>$T_{\text{max}}$ at Major degradation, °C</th>
<th>$R_{\text{max}}$, wt %/min</th>
<th>$E_a$, Horowitz-Metzger Method, kJ/mol</th>
<th>$E_a$, Freeman-Carroll method, kJ/mol</th>
<th>Order of Reaction, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy-HDPE fabric</td>
<td>218</td>
<td>309</td>
<td>388</td>
<td>47.1</td>
<td>30.765</td>
<td>29.230</td>
<td>0.631</td>
</tr>
<tr>
<td>EP-HDPE fabric -0.1phr clay</td>
<td>289</td>
<td>325</td>
<td>380</td>
<td>111.2</td>
<td>20.877</td>
<td>23.298</td>
<td>0.688</td>
</tr>
<tr>
<td>EP-HDPE fabric -0.2 phr clay</td>
<td>276</td>
<td>323</td>
<td>379</td>
<td>175.5</td>
<td>29.259</td>
<td>25.341</td>
<td>0.765</td>
</tr>
<tr>
<td>EP-HDPE fabric -0.3phr clay</td>
<td>259</td>
<td>308</td>
<td>373</td>
<td>89.7</td>
<td>25.424</td>
<td>25.291</td>
<td>0.48</td>
</tr>
<tr>
<td>EP-HDPE fabric -0.5phr clay</td>
<td>255</td>
<td>295</td>
<td>370</td>
<td>79.3</td>
<td>23.139</td>
<td>25.665</td>
<td>0.391</td>
</tr>
<tr>
<td>EP-HDPE fabric -0.7phr clay</td>
<td>254</td>
<td>308</td>
<td>386</td>
<td>134.5</td>
<td>30.052</td>
<td>24.391</td>
<td>0.604</td>
</tr>
</tbody>
</table>

The kinetic parameters including activation energy values evaluated from different models have been shown in Table 5.1. Both these kinetic theories have shown a decrement with the addition of clay. The thermal analysis gives an impression that the thermal stability of epoxy-HDPE-clay composite laminates depend on the clay composition. The slight increase in IDT and $T_{\text{max}}$ from neat sample to clay reinforced epoxy-HDPE laminates during maximum rate of degradation shows increase in thermal resistance. The order ‘n’ of the degradation reaction evaluated from Freeman-Carroll method shows that the degradation reactions are not of first order (Table 5.1). Correlation values of linear fit of the data according to Horowitz-Metzger method range from 0.996 to 0.998, while those for Freeman-Carroll method range from 0.985 to 0.992. Hence both the methods are quite acceptable; however Horowitz-Metzger method was found to be more relevant.

### 5.3.3 Flame Retardant Properties
To know the flame retardant properties of the composite laminates UL-94 Horizontal Burning and Vertical Burning tests were conducted as per the Underwriters Laboratory procedure [Under Writers Laboratory Manual, 1982]. Flame retardancy tests with Horizontal Burning have shown that introduction of clay particles reduces the linear burning rate from 16 mm/min for neat epoxy – HDPE fabric laminate to 7.5 mm/min for 0.1 phr clay reinforcement. This has been further reduced upto 4.0 mm/min for 0.7 phr clay reinforcement (Figure 5.9). All the samples including neat samples have linear burning rate much below the limiting value of 75 mm/min (for horizontal burning test, a material should not have a burning rate exceeding 75 mm per minute over a 75 mm span for specimens having a thickness less than 3.0 mm.). Clay particles while burning have produced noncombustible gases contributing to the flame retardancy of the polymeric matrix. The noncombustible gases decrease the burning rate and reduce the heat release during the combustion [Mauro Zammarano et al., 2005; Camino G et al., 2001]. Clay particles may be acting as barriers for the flame propagation and increased char yield might have decreased the burning rate. However UL-94 Vertical Burning tests for these samples showed burning over 30 sec after the removal of flame with dripping which ignited the cotton kept 300mm below the sample which is a failure of V0, V1 and V2 tests. The results of UL-94 tests indicate that the materials can be used for construction, agriculture and decorative purposes [Underwriters Laboratories, 29JAN01, ISBN 0-7629-0082-2].
5.3.4 Morphological Properties

In order to establish the dispersion characteristics of prepared composite composites the morphological features of fractured surfaces of impact broken samples has been observed using scanning electron microscopy. The observed microscopic images revealed a good dispersion of clay particles at low clay loading (Figures 5.10b, and 5.10c) and agglomeration build up at higher clay loading (Figures 5.10d, 5.10e and 5.10f). In neat epoxy – HDPE sample the fiber pullout is relatively low compared to other samples (Figures 5.10a). However fiber pullout perpendicular to the impact direction has increased with the increase in clay content. As the clay content increased beyond 0.2 phr clay, the agglomeration or the tactoids of clay particles formed has

Figure 5.9 Reduction of burning rate with the increase in clay loading.
decreased the strength between matrix and the fiber resulting in the initiation of cracks.

Figure 5.10a  SEM of Neat Epoxy-HDPE Composite Laminate  
Figure 5.10b  SEM of Epoxy-HDPE-0.1 phr Clay Composite Laminate

Figure 5.10c  SEM of Epoxy-HDPE-0.2 phr Clay Composite Laminate  
Figure 5.10d  SEM of Epoxy-HDPE-0.3 phr Clay Composite Laminate
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Figure 5.10e  SEM of Epoxy-HDPE-0.5 phr Clay Composite Laminate
Figure 5.10f  SEM of Epoxy-HDPE-0.7 phr Clay Composite Laminate

Figure 5.11  Photograph of a Sample of Epoxy – HDPE Fabric – Clay Composite Laminate
5.4 Conclusion:

The tensile, impact and flame retardancy behaviors of the composite laminate samples with different organoclay loadings were investigated. From the tensile and impact tests, it was found that the tensile and flexural strength, Young’s modulus and impact resistance of the composite laminates increased with the increase of organoclay loadings. However, these properties decreased as the organoclay loading was raised beyond 0.2 phr. Elongation at break has not been improved greatly by the addition of clay, which might be due to the rigidity of clay structures that has limited the plastic deformation of matrix. Thermal stability of the material was found to decrease slightly with the clay addition. The improved mechanical properties are obtained at the expense of slightly decreased thermal stability. At higher clay loading clay particles agglomerate, act as stress concentrators and initiate cracking hence decreasing the impact and tensile strength. The decreased activation energy is possibly because of the release of the low-molecular-weight surface modifiers used in Cloisite-30B at higher temperature. The decline in burning rate in UL-94 test is attributed to the reason that the clay particles acting as barriers for the flame propagation and have increased char yield. Morphology of the broken samples indicate better dispersion at lower clay load and tactoid formation at higher clay loading.