

Thermal Degradation Kinetics, Mechanical, and Flame Retardant Properties of Epoxy-HDPE Fabric-Clay Composite Laminates

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ABSTRACT: Addition of particulates into laminates has been found to influence thermal and mechanical properties. Composite laminates of epoxy-high density polyethylene (HDPE) fabric-clay were prepared by reinforcing clay in the range of 0.1–0.7 phr into epoxy-HDPE fabric laminates. These laminates are characterized for their mechanical, thermal, and flame retardant performances. With the addition of clay, an increase was found in impact resistance, tensile strength, flexural strength, and Young's modulus to an extent of 0.2 phr clay, after which there is a decrease in these properties. The thermal stability is found to decrease with the addition of clay. The improved mechanical properties are obtained at the slight expense of thermal stability. UL-94 tests indicate a reduction in the burning rate. Morphology of the broken samples indicate better dispersion at lower clay load and tactoid formation at higher clay loading. These materials have potential applications in agriculture, construction, and decorative purposes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40751.

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INTRODUCTION

Polymer composites and their testing are integral components of modern society. Polymer laminates have been used in various fields. These materials are being used in fields such as waste containment facilities, flooring, agriculture sector, roofing, packaging, etc.¹ Low density polyethylene, medium density polyethylene, and high density polyethylene (HDPE) are some of widely used polymers in the form of flexible films and laminates for bags, semi-rigid and rigid containers, in pipe extrusion, and injection molding of different items.² 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 use the benefits of lightweight and high strength laminate materials.³ HDPE film is a good candidate as the liner material because it possesses good strength, outstanding chemical resistance, and minimal extractable matter, which might permeate and contaminate the water.⁴ 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.⁵ The laminates of flax fiber in recycled HDPE matrix have shown improvement in fracture toughness up to 20% fiber fraction.⁶ The performance of composites or laminates during utilization is related to their mechanical properties, thermal resistance, and thermal stability. These properties are engineered by suitable combination of reinforcement, polymeric matrix, and processing technique.^{7,8} Hybrid composites, such as Nylon—6,6, nanofabric interleaving in epoxy/carbon fiber have shown improved impact resistance by 60%.⁹ Epoxy—nylon laminates when loaded with low quantity of clay have shown improved mechanical properties.¹⁰ Thermoset polymer epoxy resins possess better mechanical strength, chemical resistance, and service temperature requirements, hence been used to maximum extent in many industries.^{11,12} Epoxy resins offer 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 number 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

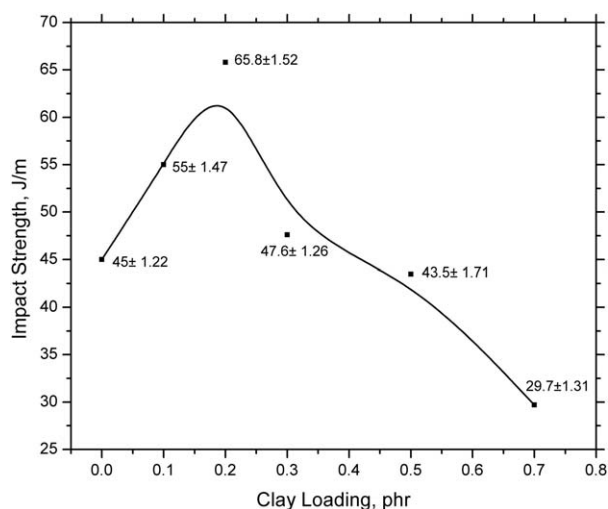


Figure 1. Impact strengths of epoxy—HDPE fabric—Clay composite laminates.

chemical additives known as flame retardants that are being used to delay the ignition and control burn. A number of halogen and phosphorous based compounds have been used as flame retardants in polymers without affecting their other properties and quality negatively. Because the halogenated compounds contaminate environment, halogen-free flame retardants have occupied the market.^{13,14} Some of inorganic flame retardants required to be reinforced at high volume loading which impact negatively on the costs, process ability, and quality of the product.^{15,16} 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 this work.

EXPERIMENTAL

Materials

Huntsman Araldite MY740 Epoxy Resin (density 1.16 g/cm³), K112 Accelerator, and Aradur HY918 Hardener (a low viscosity anhydride hardener, density 1.2 g/cm³) were procured from Huntsman Advanced Materials (India). HDPE interwoven fabric was obtained from Reliance Industries, India. The fabric had following morphological features: fibers in the fabric were of 115 μm diameter, 2500 mesh count openings per square inch, 245 μm fabric thickness, and 50 g/m². Cloisite-30B clay was procured from Southern Clay products, USA. The average particle size as given by the supplier was 10 μm with a density 1.98 g/cm³. All the chemicals were used without any modifications.

Preparation of Composite Laminates

Laminate hybrids of epoxy—HDPE fabric (5 layers) were prepared by incorporating clay particles as reinforcement with a loading of 0.1–0.7 phr using conventional hand layup technique. Initially, clay was mixed with 100 phr epoxy and stirred for 30 min 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 min at 1350 rpm. The HDPE interwoven fabrics of the size 200 mm × 100 mm 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 h and postcured at 120°C for 4 h between two iron plates.

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 D790). Tensile testing was done with a stress range 3000 MPa, 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, 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, UL-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, Quanta—200, FEI, The Netherland.

RESULTS AND DISCUSSIONS

Mechanical Properties

Neat epoxy—HDPE fabric laminates have shown the impact strength of 45 ± 1.22 J/m. When these laminates were incorporated with lower load of clay particles, they have shown improvement in impact strength. A total of 0.1 phr clay introduction into these laminates resulted in an increase of impact strength to 55 ± 1.47 J/m. When clay composition was increased to 0.2 phr, impact strength was increased to 65.8 ± 1.52 J/m (Figure 1). However, further increase in clay content into the laminates have resulted in decrease of impact strength, with 0.7 phr clay incorporated epoxy—HDPE fabric laminate showing the impact strength of 29.7 ± 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 ± 0.72 MPa and 450 ± 18 MPa, respectively, and

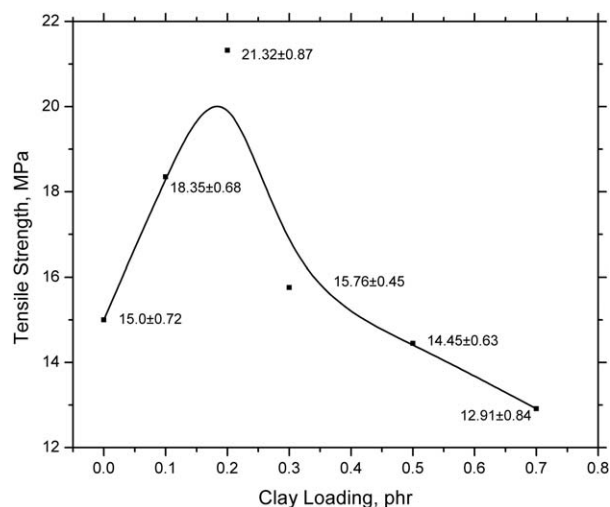


Figure 2. Tensile strengths of epoxy—HDPE fabric—Clay composite laminates.

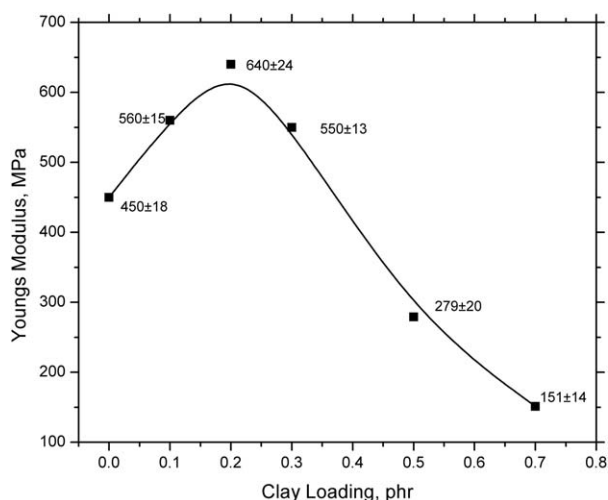


Figure 3. Young's moduli of epoxy—HDPE fabric—Clay composite laminates.

0.2 phr clay reinforced laminate sample showing the maximum values 21.32 ± 0.57 MPa and 640 ± 24 MPa, respectively. Figures 2 and 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 with the neat laminate sample. Also the flexural strength for 0.2 phr clay reinforced epoxy—HDPE fabric composite laminate showed greater improvement (54.10 ± 2.3 MPa) compared with the neat epoxy—HDPE sample (29.23 ± 1.2 MPa; Figure 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 loads onward. 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.¹⁵ The smaller particles at lower clay load, being more finely dispersed throughout the matrix,

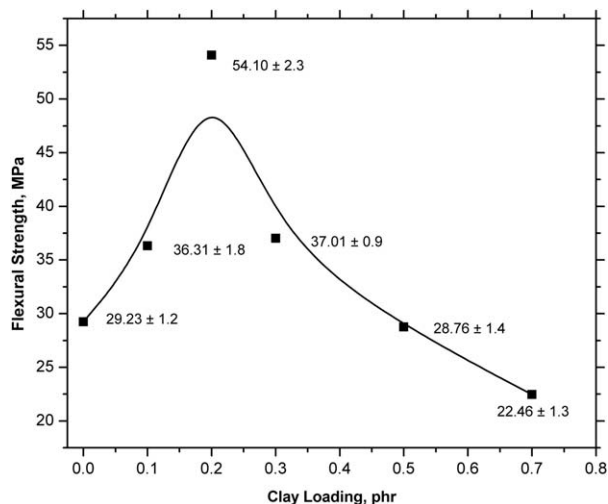


Figure 4. Flexural strength of epoxy—HDPE fabric—Clay composite laminates.

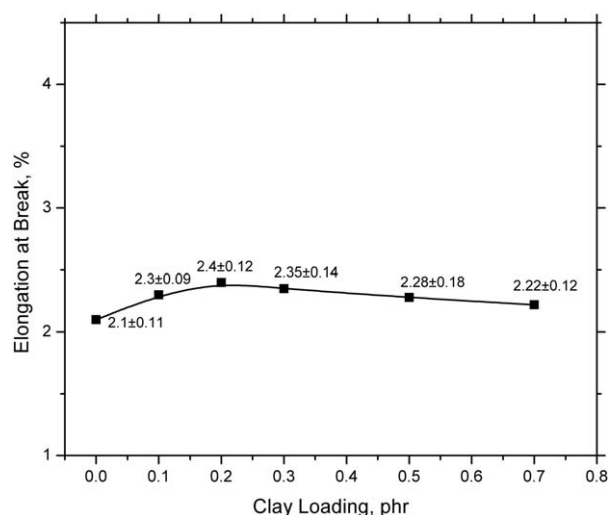


Figure 5. Percentage elongation at break of epoxy—HDPE fabric—Clay composite laminates.

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.^{16,17}

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 interfacial bond strength due to the addition of organoclays.¹⁸ On the other hand, decrease in trend at higher loading is probably due to the formation of agglomerates or tactoids content that 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.¹⁷

The percentage elongation has shown marginal increase from $2.1 \pm 0.11\%$ for neat sample to a maximum of $2.4 \pm 0.12\%$ (for 0.2 phr clay reinforcement), later which is decreased marginally with the increased clay loading (Figure 5). This may be due to the rigidity of clay structures which might have limited the plastic deformation of the polymer matrix.¹⁹

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 such as epoxy and unsaturated polyester composites.^{5,10,17,20} The initial degradation temperature (IDT) sometimes used to understand thermal stability of materials is taken at which weight loss reaches 5%.¹⁷ 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 I. 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 (Figure 6). This may be due to the good adhesion between clay and epoxy, hindering the heat propagation thereby reducing degradation rate.¹⁸

The Horowitz—Metzger integral kinetic method²¹ and Freeman and Carroll²² were applied to calculate the kinetic parameters.

Table I. Thermal Properties of Epoxy-HDPE-Clay Composite Laminates

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

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:

$$\ln \left\{ \ln \left(\frac{1}{1-\alpha} \right) \right\} = \frac{E_a \theta}{RT_e^2} \quad (1)$$

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 “ α ” is the heating rate.

Thus, a plot of $\ln \left\{ \ln \left(\frac{1}{1-\alpha} \right) \right\}$ against θ should give a straight line whose slope gives E_a (Figure 7).

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

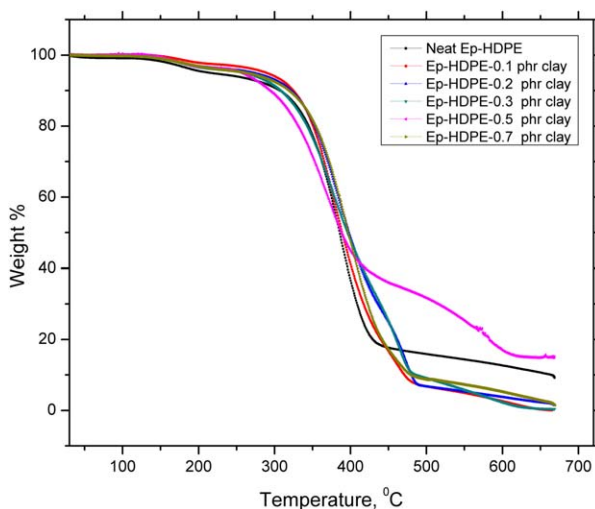


Figure 6. Thermograms of epoxy-HDPE and epoxy-HDPE-Clay composite laminates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = n - \frac{E_a}{2.303R} \frac{\Delta(1/T)}{\Delta \log W_r} \quad (2)$$

where dw/dt = rate of change of weight with time, W_r = 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, and T = temperature. The plot between the terms $\frac{\log(dw/dt)}{\log W_r}$ versus $\frac{1/T}{\log W_r}$ 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 8).

For both kinetic methods, the calculations have been done in the temperature range of 350–410°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

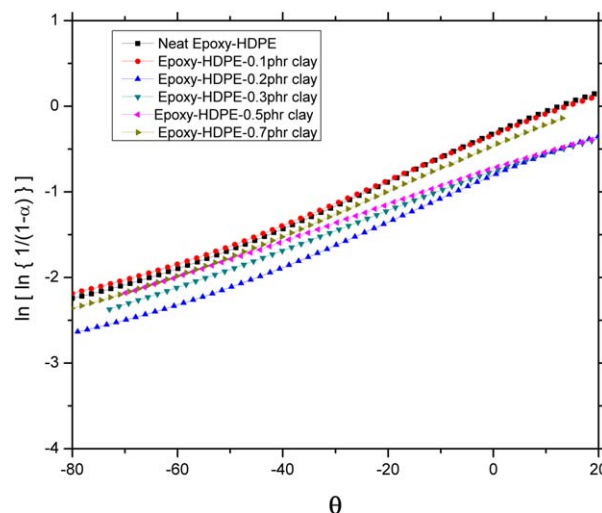


Figure 7. Horowitz-Metzger kinetic plot to find activation energy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

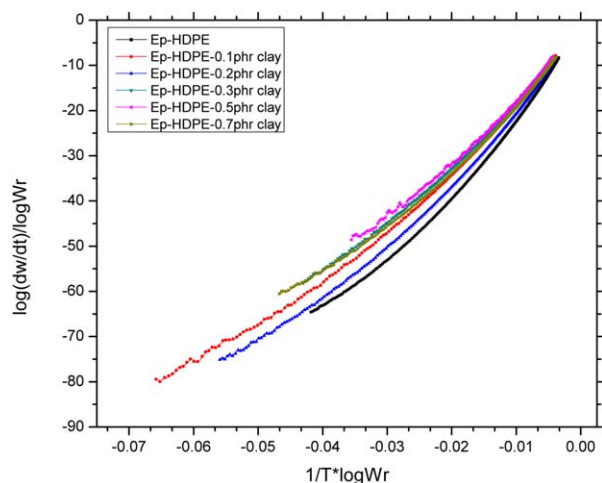


Figure 8. Freeman–Carroll kinetic plot to find activation energy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

behaviors, Table I lists the derivative peak rate of decomposition of the samples along with other thermal degradation properties. The IDT, which is generally considered to understand the thermal stability of a material,¹⁷ 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 is 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–Carroll method are ranging from 29.230 kJ/mol to 24.391 kJ/mol.

The maximum rate of degradation, R_{\max} , is another parameter used to understand the effect of filler on degradation behavior of a polymer.²⁰ With the increase in clay content, the maximum rate of degradation, R_{\max} , has increased and the activation energy (E_a) for laminate hybrids are marginally less than that of neat sample. Also the R_{\max} values for higher order clay addition have been inconsistent. 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 organo modified clay.¹⁰

The kinetic parameters including activation energy values evaluated from different models have been shown in Table I. Both these kinetic theories have shown a decrement in E_a values 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_{\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 I). Correlation values of linear fit of the data according to Horowitz–Metzger method range from 0.996 to 0.998, whereas 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.

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.²³ 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 up to 4.0 mm/min for 0.7 phr clay reinforcement (Figure 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.^{24,25} 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 s after the removal of flame with dripping which ignited the cotton kept 300 mm 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.²³

Morphological Properties

To establish the dispersion characteristics of prepared 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

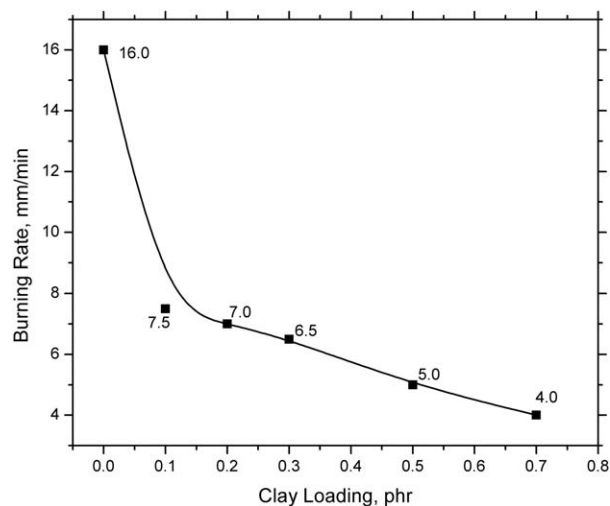


Figure 9. Reduction of burning rate with the increase in clay loading.

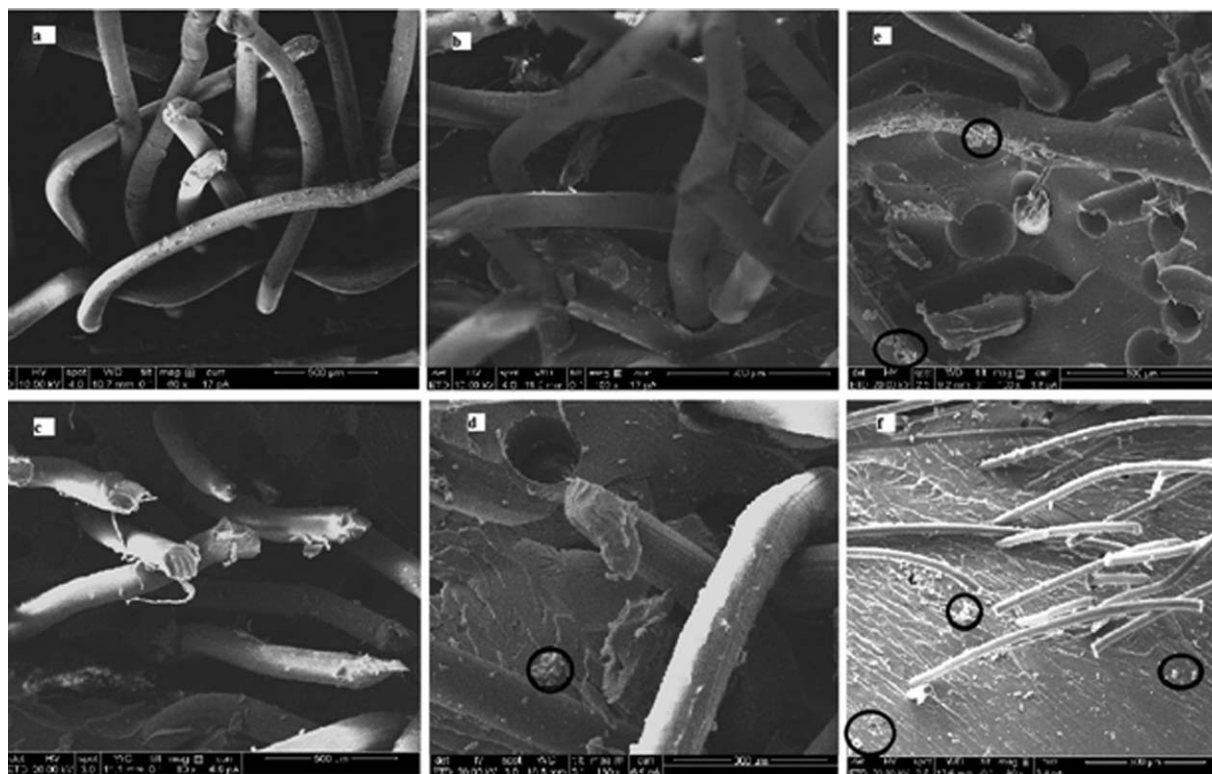


Figure 10. SEM of (a) neat epoxy-HDPE, (b) epoxy-HDPE—0.1 phr clay composite laminate, (c) epoxy-HDPE—0.2 phr clay composite laminate, (d) epoxy-HDPE—0.3 phr clay composite laminate, (e) epoxy-HDPE—0.5 phr clay composite laminate, and (f) epoxy-HDPE—0.7 phr clay composite laminate.

dispersion of clay particles at low clay loading [Figure 10(b,c)] and agglomeration build up at higher clay loading [Figure 10(d–f)]. In neat epoxy—HDPE sample [Figure 10(a)], the fiber pullout is relatively low compared with other samples. 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 decreased the strength between matrix and the fiber resulting in the initiation of cracks.

CONCLUSION

The tensile, impact, and flame retardancy behaviors of the epoxy—HDPE fabric—clay 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 acted as barriers for the flame propagation and have increased the char yield. Morphology of the broken samples indicates better dispersion at lower clay load and tactoid formation at higher clay loading.

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