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Synergistic effect of clay and polypropylene short fibers in epoxy based ternary composite hybrids

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Abstract. Polypropylene short fiber (PP)-clay particulate-epoxy ternary composites were prepared by reinforcing PP short fiber and clay particles in the range of 0.1 phr to 0.7 phr into epoxy resin. Prepared hybrid composites were characterized for their mechanical, thermal and flame retardant properties. The obtained results indicated an increase in impact resistance, tensile strength, flexural strength and Young's modulus to an extent (up to 0.5 phr clay and 0.5 phr PP short fiber) and then decreases as the reinforcing phases are further increased. The thermal stability of these materials are found to increase up to 0.2 phr clay and 0.2 phr PP addition, beyond which it is decreased. Addition of clay is found to have the negative effect on epoxy-PP short fiber composites, which is evident from the comparison of mechanical and thermal properties of epoxy-0.5 phr PP short fiber composite and epoxy-0.5 phr PP short fiber-0.5 phr clay composite hybrid. UL-94 tests conducted on the composite hybrids have showed a reduction in the burning rate. Morphological observations indicated a greater fiber pull with the addition of clay. The performed tests in the present study indicated that materials under investigation have promising applications in construction, agriculture and decorative purposes.

Keywords: hybrid; synergistic effect; flame retardance; mechanical properties; thermal properties

1. Introduction

Among the polymer composites, fiber reinforced composites have become key players in automotive and aerospace industry. They are prepared by reinforcing fibers (either short or long fibers) into the polymeric matrix. Of the several composites, carbon fiber reinforced epoxy composites have established themselves in the industry due to their high modulus, high strength, stiffness and creep resistance (Wang and Garton 1992). However, these composites are susceptible for impact damage. There are several studies involving polypropylene as a matrix and clay as

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reinforcing component. Addition of clay into the polypropylene matrix has increased strength and stiffness, but the fracture behavior has shown a transition from ductile to brittle and decreased toughness of materials (Chen *et al.* 2003). Composites of polypropylene short fibers reinforced epoxy have shown improved thermal stability (Prabhu *et al.* 2007). The presence of two reinforcing phases in a composite can change the properties of the composite based on the contributions of the constituents. Such variations are called hybrid effects and can be positive or negative from the properties predicted by the rule of mixtures (Peijs *et al.* 1990a, b). Polypropylene-Poly (ethylene propylene)-poly (ethylene vinyl acetate) hetero-phase matrix when reinforced with organoclay at higher load of 6 wt% has improved flame retardant properties (Zaragoza *et al*. 2006). Polypropylene fiber and mercapto-modified polypropylene blend fiber (PPEVASH) combined with carbon fiber reinforced epoxy hybrids have resulted in increased impact resistance (Dutra *et al*. 2007). Several other studies on hybrids involving epoxy-carbon-polypropylene and carbon-Kevlar-bismaleimide have shown improvement in material properties (Peijs *et al*. 1990b, c, d, Jang and Moon 1995, Wan *et al*. 2007). Polyethylene fibers when reinforced into epoxy-carbon fabric laminates have improved post crush structural integrity, whereas the individual polyethylene – epoxy and carbon fabric-epoxy composites have failed to retain their structural integrity after crushing (Peijs *et al*. 1990d). Some of the studies have shown a reduction in tensile, impact strength and fracture toughness of polymer clay composites with the addition of clay particles (Alexandre and Dubois 2000, Peeter Broeck *et al*. 2005, Zhao *et al*. 2005). Very few studies have indicated the usefulness of short fiber – particulate reinforced composite systems. It has been reported that introduction of fly-ash along with short fibers as reinforcement in epoxy results in retention of the strength and modulus in contrast to the short fiber-epoxy system (Kulkarni and Kishore 2003). At higher fiber loading introduction of fly-ash has been found to decrease the strength of the composite. Addition of clay to PP-glass short fiber system imparts improved thermal stability, tensile and flexural strength (Normasmira *et al*. 2013). In another study addition of nano-clay into HDPE-glass short fiber system yielded improved tensile and wear properties (Mohan and Kanny 2012). To gain more insight into the short fiber-particulate-epoxy ternary composites, the preparation of polypropylene (PP) short fibers-clay reinforced epoxy ternary composite hybrids was carried out in the present work. The mechanical, thermal and flame retardant properties are discussed in this paper.

2. Experimental section

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. Polypropylene fibers were obtained from Reliance Industries Limited, INDIA. Average fiber length was 3 mm and average diameter was 40 µm. 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.

2.2 Preparation of composite hybrids

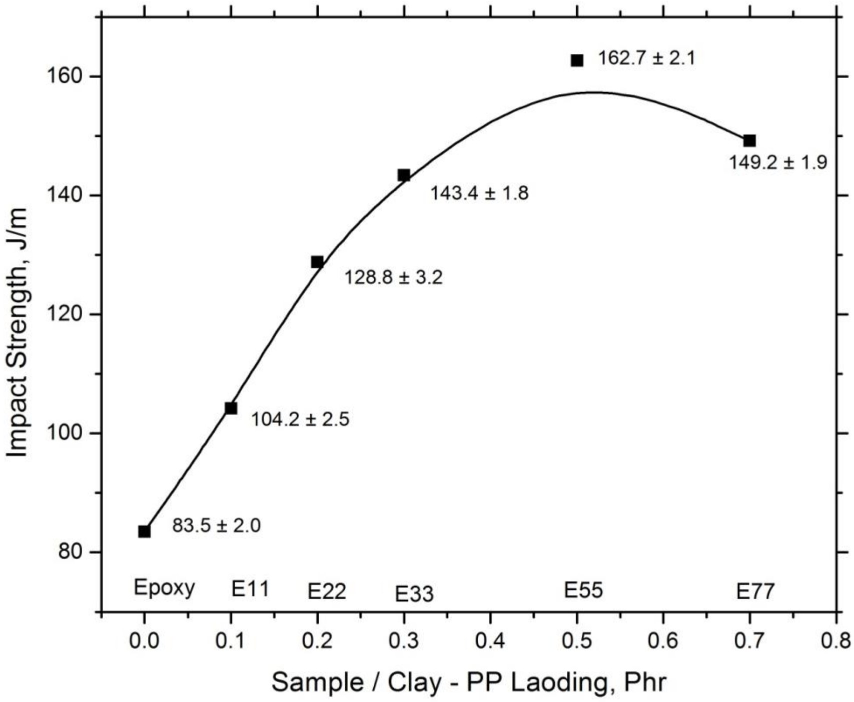

Fig. 1 Impact strengths of epoxy-PP short fibers-clay composites

Composites of epoxy-PP short fibers-clay were prepared by incorporating Cloisite-30B clay particles and 3 mm PP short fibers as reinforcements with a composition ranging from 0.1 phr to 0.7 phr using conventional open mold technique. Initially clay and PP short fibers were mixed with 100 phr epoxy and stirred for 30 minutes at 1350 rpm using a conventional variable speed TANCO stirrer (PLT-184). Then 1 phr accelerator and 85 phr hardener were mixed with epoxy – PP-clay mixture for another 5 minutes at 1350 rpm. The contents were transferred to a Teflon mold of the size 200 mm×100 mm×3 mm. The mixture was then degassed in a vacuum oven for 1 h at 60℃. Then samples were cured at 100℃ for 2 hours and post cured at 120℃ for 4 hours.

2.3 Material characterization techniques

Izod Impact test (ASTM D256) for ternary composite hybrids was conducted using Tinius Olsen IT504 Impact Tester. UTM, Hounsfield, H50km, UK, was used for tensile testing (ASTM D638) and flexure testing (ASTM D 790). Tensile testing was done with a stress range 3000 MPa, strain range 300% and speed 5 mm/min, whereas flexural testing was performed in three point bending 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℃ at a heating rate of 10℃ per min. in a 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 Under Writers Laboratories, USA.

Morphology of impact broken samples was investigated using Environmental Scanning

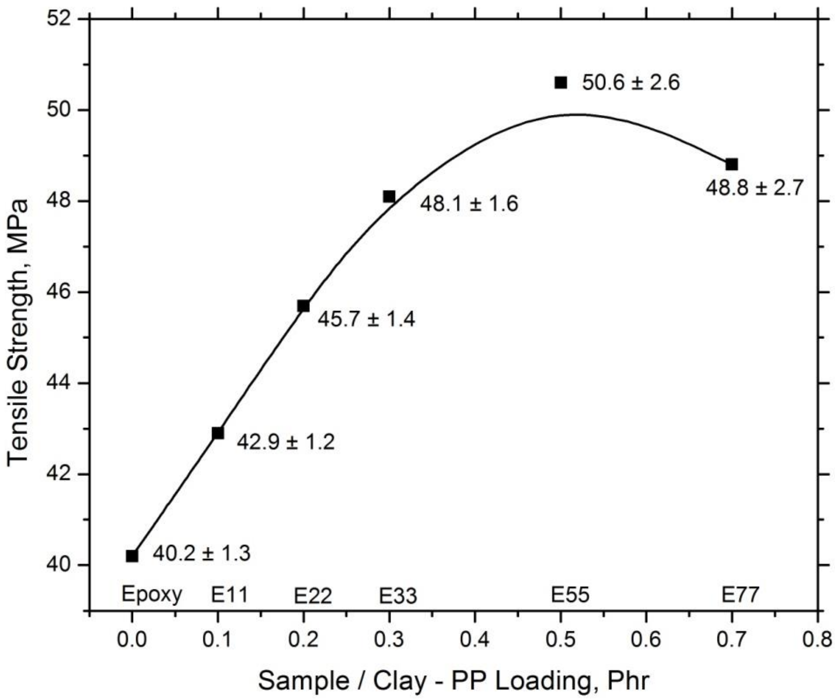

Fig. 2 Tensile strengths of epoxy-PP short fibers -clay composites

Electron Microscope, ESEM, Quanto-200, FEI, Netherland.

3. Results and discussions

3.1 Mechanical properties

Cured neat epoxy has shown the impact strength of 83.5±2.0 *J*/m. When the epoxy was incorporated with combined reinforcement of lower load of PP short fibers and clay particles, the composite materials have shown improvement in impact strength up to 0.5 phr (Fig. 1). However a further increase of both these reinforcements into the epoxy has resulted in the decrease of impact strength.

Tensile strength and Young's modulus for the samples have shown the similar trend with neat epoxy showing 40.2±1.3 MPa and 2560±10.1 MPa, respectively. The epoxy with 0.5 phr composition (E55) has shown the maximum tensile strength (26 %) and Young's modulus (20 %) values. Figs. 2 and 3 depict the tensile strength and Young's modulus values respectively for all hybrid composites. Also the flexural strength for the E55 composite hybrid showed an improvement of 36% compared to the neat epoxy sample (Fig. 4). And the elongation at break was found to decrease with the addition of reinforcements (Fig. 5).

An increase in impact strength was observed with the addition of reinforcements (up to 0.5 phr of PP short fibers and Clay), and decreased above that composition. Similar trend was reported by Zhao *et al*. (2005) for polyethylene fiber reinforced epoxy. Based on this report it is suggested that

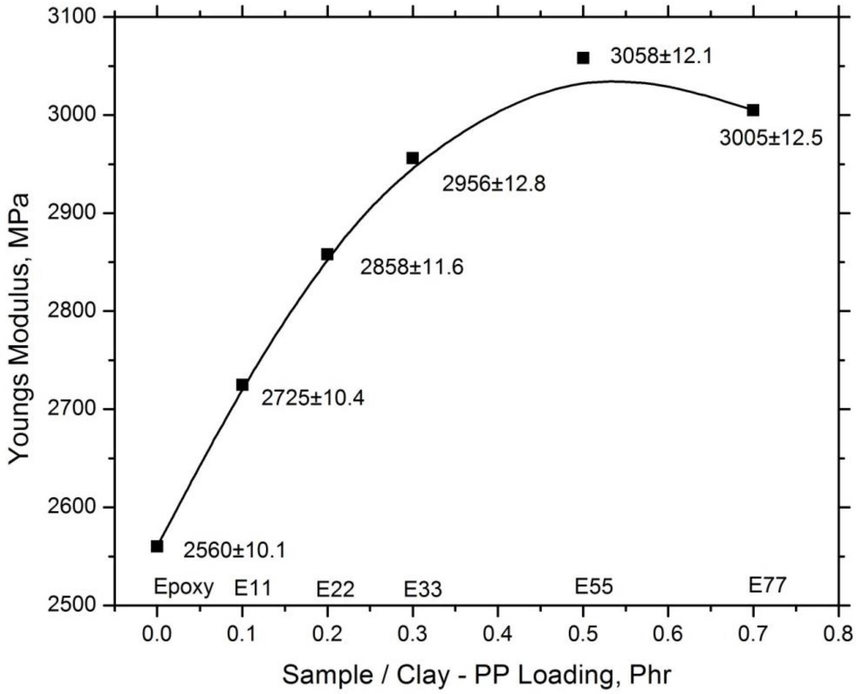

Fig. 3 Young's modulus of epoxy-PP short fibers-clay composites

the increase in impact strength is due to better dispersion of reinforcements at lower loading. The direction of crack path is deviated by the presence of dispersed reinforcements and twisted, crack growth deflection has contributed to the increased energy consumption (Zhao *et al*. 2005). The PP short fibers in the epoxy matrix have consumed extra energy. During the fracture process of composites, there might be difference between the breaking strains of the constituents, each fiber might have broken repeatedly with increasing strain on the structure before overall failure. This fragmentation process builds up tension, carry loads again and again, contribute towards increased strength until the length of fiber reaches a minimum or critical value (Harlow 1983). Morphological observations suggest that, lower loading of clay particles have decreased the tendency of bunching of fibers and increased the strength (Kulkarni and Kishore 2003). Also 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. However, at higher clay loading clay particles tend to agglomerate and act as stress concentrators and eventually decrease the impact strength (Laoutid *et al*. 2009, Ozava *et al*. 1996). This agglomeration also leads to lowering of clay surface area and eventual decrease in polymer/clay surface interaction which results in decrease in strength (Azeez *et al*. 2013).

The increase in tensile strength, flexural strength and Young's modulus in the composite hybrids at lower clay loading could be attributed to the improved interfacial bonding strength due to the addition of organoclays (Yasmin *et al*. 2006). The presence of clay particles has decreased the tendency of PP fiber to bunch; in turn it has improved these properties (Kulkarni and Kishore 2003). On the other hand, a decrease in trend at higher loading is due to the formation of agglomerates or tactoids content, that cannot act efficiently in dissipating mechanical energy, but

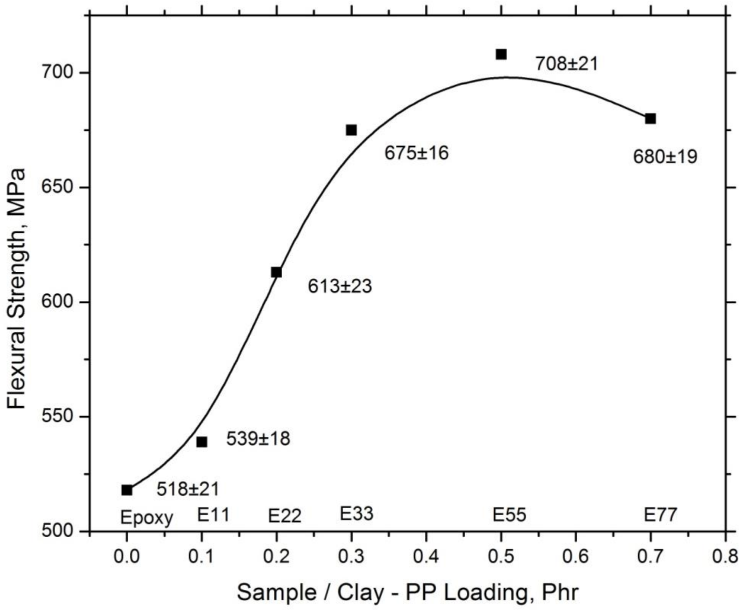

Fig. 4 Flexural strength of epoxy-PP short fibers -clay composites

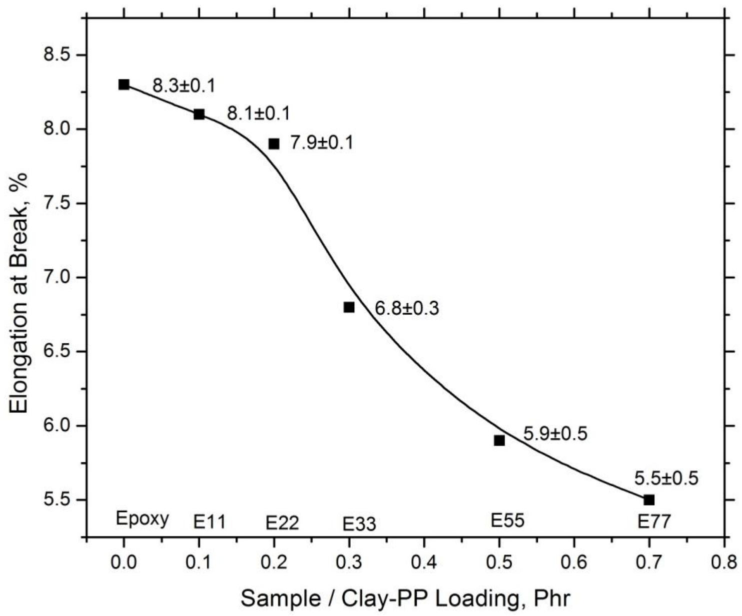

Fig. 5 Elongation at break of epoxy-PP short fibers -clay composites

instead have served as flaws or defects and crack initiation sites decreasing the properties (Kulkarni and Kishore 2003).

The percentage elongation has shown a decreasing trend (reduced by 33 % for E77 composite hybrid compared to neat epoxy) with the increased reinforcement (Fig. 5). This is due to the PP

Table 1 Mechanical and flame retardant properties of E50 and E55 composites

Sample code / composition	Impact Strength, *J*/m	Tensile strength (MPa)	Youngs modulus (MPa)	Flexural strength, (MPa)	Elongation @ break (%)	Burning rate, mm/min
E50, Epoxy-0.5phr PP	170.3±2.3	56.2±1.8	3202±11.9	732±14	9.1±0.9	4.0
E55, Epoxy-0.5phr PP-0.5phr Clay	162.7±2.1	50.6±2.6	3058±12.1	708±21	5.9±0.5	3.4

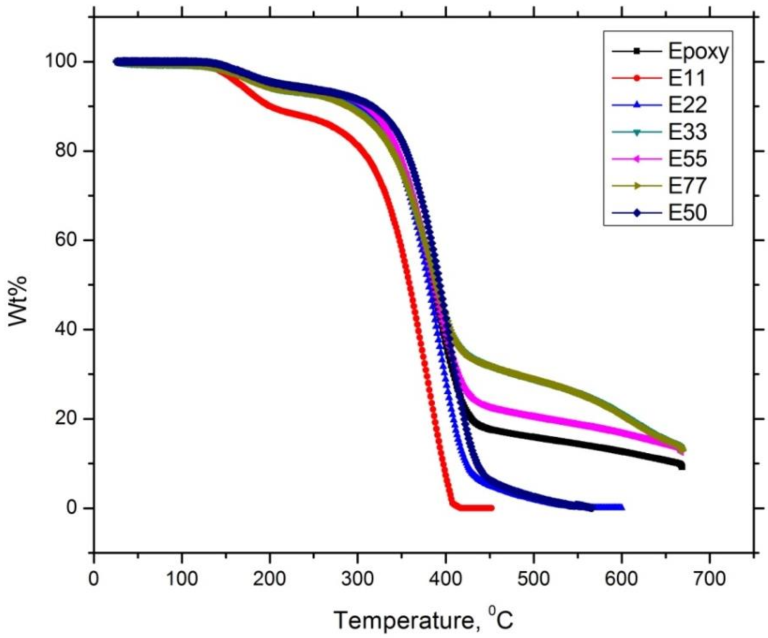

Fig. 6 Thermograms of epoxy-PP short fibers-clay composites

short fibers pull out and the rigidity of clay structures which has limited the plastic deformation of the polymer matrix (Chen *et al*. 2003).

To find the synergistic effect of clay and PP short fibers, a sample of epoxy containing 0.5 phr PP short fibers only (E50) as reinforcement was tested for mechanical performance. This was chosen because E55 composite hybrid composite containing 0.5 phr each of PP short fibers and clay reinforcement has yielded better mechanical properties. The aim was to understand whether the addition of clay affects the mechanical performance of PP short fibers-epoxy composite system or not. The impact, tensile and flexural strength, Young's modulus and elongation at break were found and listed in Table 1. It has been observed that the addition of clay into PP short fibers-epoxy system has adversely affected the mechanical performance. The impact strength, tensile strength, Young's modulus and flexural strength of E50 is better than that of E55. With the addition of clay, the strength of the epoxy-PP short fiber composites is decreasing. This is due to clay particles acting as crack initiation sites that extend the crack along the fibers. Also at higher fiber content bunching of fibers creep in decreasing the mechanical performance of the composite

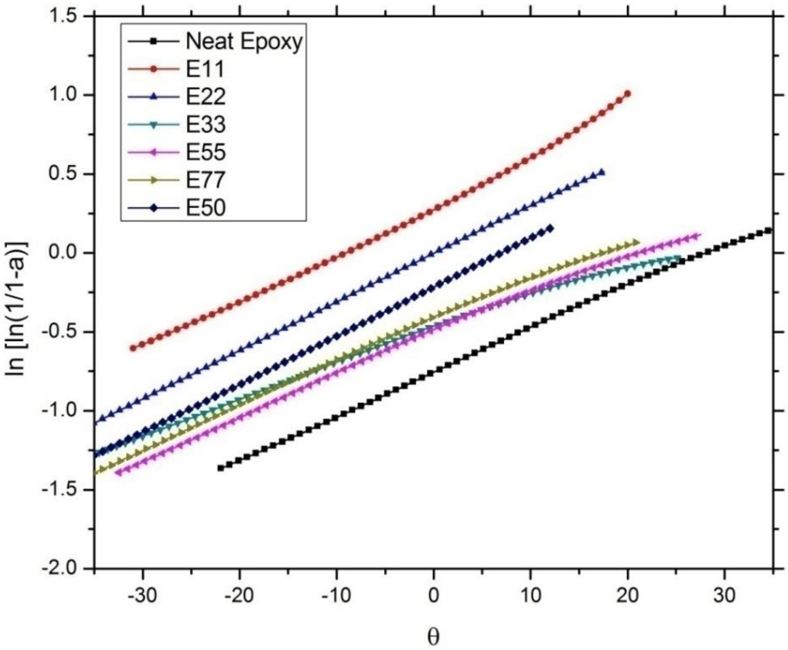

Fig. 7 Horowitz-Metzger kinetic plot to find E_a of epoxy-PP short fibers-clay composites

hybrids. However elongation at break for E50 is slightly more than the neat epoxy sample and E55 sample. The fibers have undergone more fragmentation process that consumes more energy, increasing the percentage elongation at break.

3.2 Thermal properties

TGA was carried out at a 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 the thermal stability of materials is taken at which weight loss reaches 5% (Kulkarni and Kishore 2003). 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 cured neat epoxy and the composite hybrids are given in Table 2.

The Horowitz-Metzger integral kinetic method (Horowitz and Metzger 1963) and Freeman and Carroll method (Freeman and Carroll 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

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

Where E_a=energy of activation, θ=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,

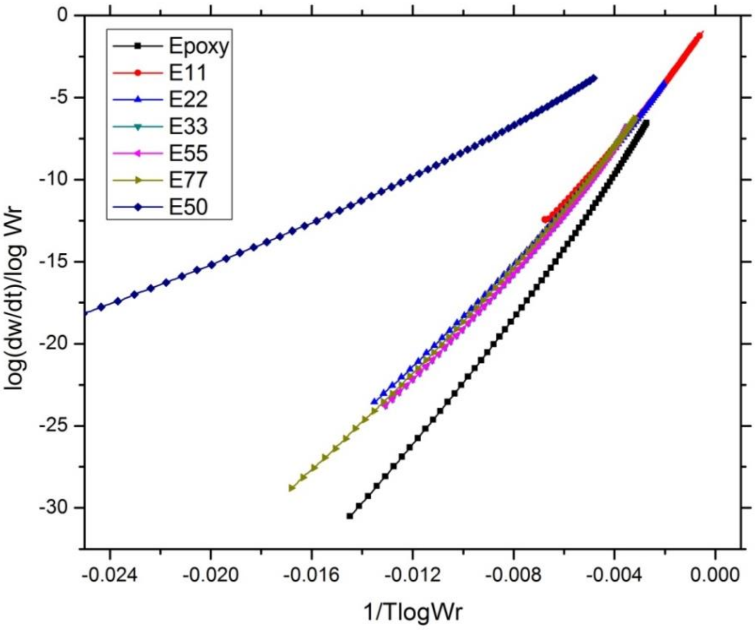

Fig. 8 Freeman-Carroll kinetic plot to find E_a of epoxy-PP short fibers -clay composites

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 (Fig. 7).

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

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

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, '*R*' is universal gas constant, 8.314 kJ/mol/K, *n*=order of reaction, *T*=Temperature.

The plot between the terms $\frac{\log(dw/dt)}{\log W_r}$ vs $\frac{1/T}{\log W_r}$ 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*) (Fig. 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.

Activation energy values evaluated by the Horowitz-Metzger method and Freeman-Caroll method are ranging from 24.402 kJ/mol to 41.837 kJ/mol.

The maximum rate of degradation, R_{max} is another parameter used to understand the effect of reinforcement on degradation behavior of a polymer (Niranjana Prabhu *et al*. 2007). Both the kinetic theories have shown increase in E_a values up to 0.2 phr clay and PP short fiber addition and thereafter a decrease in E_a values. There is an increase in T_{max} from neat sample to clay reinforced

Table 2 Thermal properties of epoxy-PP short fibers-clay composite hybrids

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	225	307	381	450.7	33.570	32.901	1.553
E11	165	200.2	386	136.45	37.683	36.016	1.310
E22	197.6	303.5	392.5	121.88	39.078	39.591	1.143
E33	189.7	290.7	389.27	128.4	33.927	34.099	1.202
E55	204	295	384.6	101.39	26.453	32.108	1.535
E77	187	286	375.1	182.78	24.402	28.308	1.422
E50	210	316	398	97.6	40.230	41.837	1.452
				R^2 Values	0.99534 to 0.9992	0.9974 to 0.9989	

epoxy-PP short fiber composite hybrids, however it is decreased after 0.2 phr reinforcement onwards. The order '*n*' of the degradation reaction evaluated from Freeman-Caroll method shows that the degradation reactions are not of the first order (Table 2). However, there is inconsistency in initial degradation temperatures of composites which might be due the degradation of low-molecular-weight surface modifiers used for modification of clay particles. Among the composite hybrids E22 composite hybrid sample has shown better thermal stability (Activation energy, E_a value is high among clay reinforced composite hybrids) and further increase in reinforcement has decreased thermal stability. This is due to the good adhesion between PP short fiber and epoxy promoted by clay at lower clay loading, hindering the heat propagation thereby reducing the degradation rate (Yasmin *et al*. 2006). Also the clay particles may be acting as binders increasing interfacial adhesion between PP short fibers and epoxy. Adhesion between epoxy and PP short fibers could have restricted segmental motion resulting in increase of thermal stability. However the introduction of clay particles with higher load has led to decrease in thermal stability of PP short fibers – epoxy composite system. At higher clay loading, as the temperature is increased the low molecular weight surface modifiers used for clay modification get released faster accelerating the degradation. Addition of clay particle into epoxy-PP short fibers composites resulted in negative synergism which is evident from comparison of the initial degradation temperature and activation energy values for E50 and E55 sample (Table 2). T_{max} and activation energy is more for E50 sample showing more thermal stability than other samples. The thermal analysis gives an impression that the thermal stability of epoxy-PP short fibers-clay composite hybrids depend on the clay composition and addition of clay into epoxy-PP short fiber composites result in decrease of thermal stability.

Correlation values of linear fit of the data according to Horowitz-Metzger method range from 0.99534 to 0.9992, while those for Freeman-Caroll method range from 0.9974 to 0.9989. Hence, both the methods are quite acceptable.

3.3 Flame retardant properties

To know the flame retardant properties of the composite hybrids UL-94 Horizontal Burning

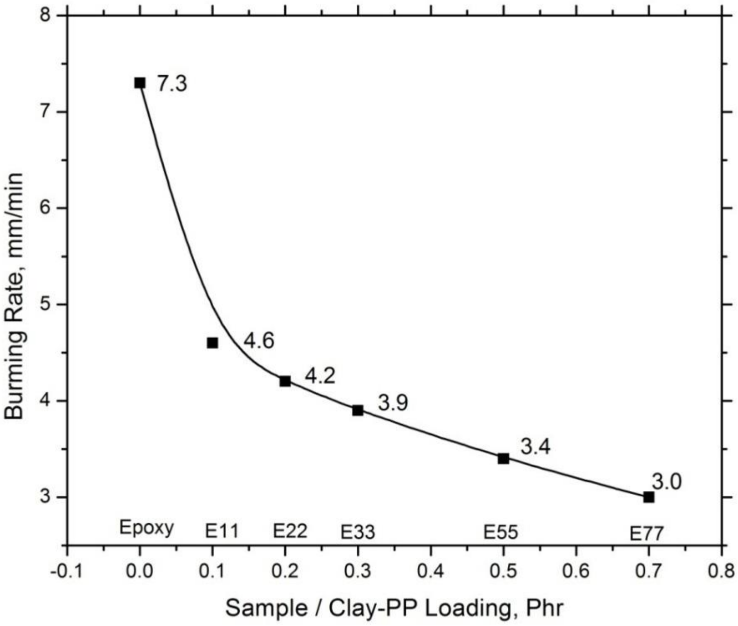

Fig. 9 Burning rates of epoxy-PP short fiber-clay composites

(HB) and Vertical Burning (VB) tests were conducted as per the Underwriters Laboratory procedure (UL 94 test for flammability, 1997). Flame retardancy tests with HB have shown that introduction of clay particles reduces the linear burning rate (Fig. 9). However E50 sample has shown a high burning rate compared to E55 (Table 1).

Here all the samples have passed UL-94 HB test. 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 (Zammarano *et al*. 2005, Camino *et al*. 2001). Clay particles thermally insulate and produce low permeable char residue of clay layers at the outer surface of the composite during combustion and act as barriers by reducing heat and mass transfer between the flame and matrix. The char residue of clay will also reduce the oxygen uptake and the escape of volatile gases produced by polymer degradation (Blumstein 1965). Also the tortuous paths created by clay galleries have retarded the burning rate by retarding the diffusion of gas molecules through the polymer matrix (Azeez *et al*. 2013). However, all the samples have failed in UL-94 VB test. Samples kept burning, but without flaming drips, 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 (UL 94 test for flammability, 1997).

3.4 Morphological studies

Scanning electron microscopy was used to understand the morphological features of fractured

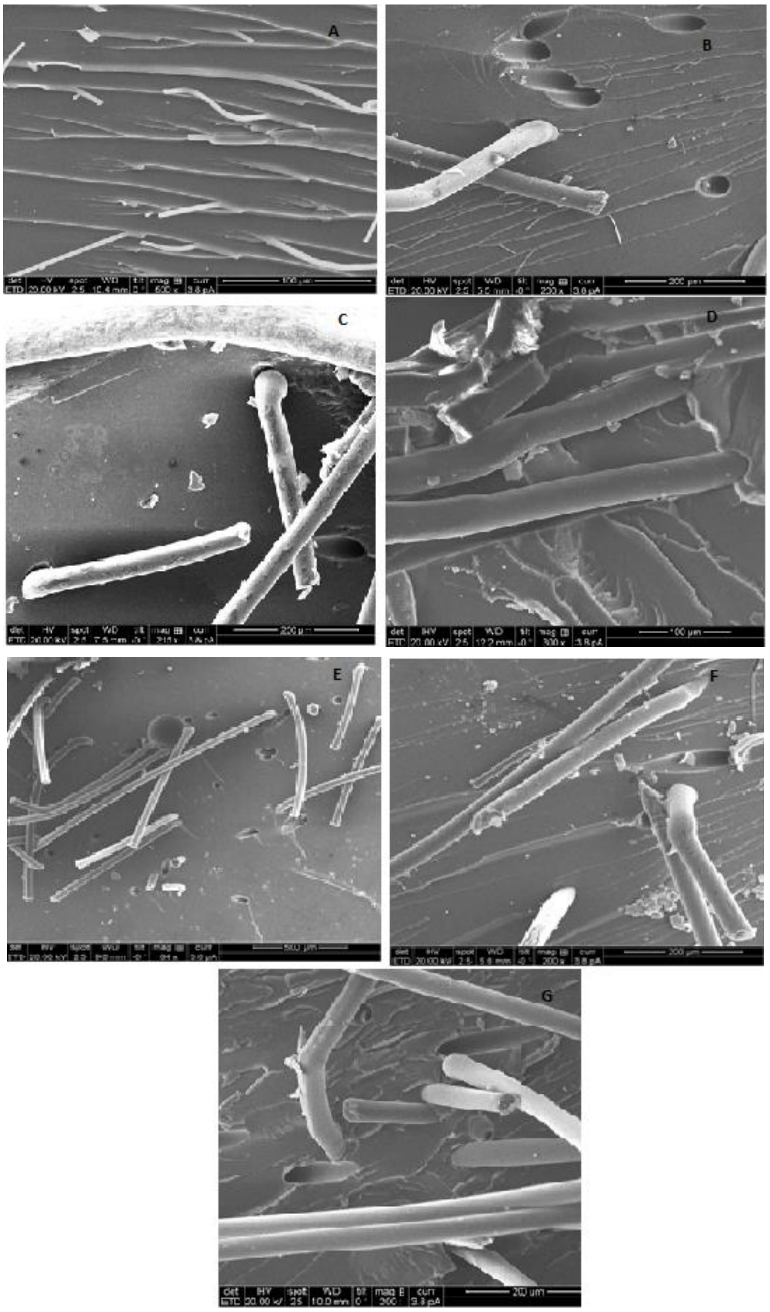

Fig. 10 Scanning electron micrographs of (A) Neat Epoxy, (B) E11, (C) E22, (D) E33, (E) E55, (F) E77 and (G) E50

surfaces of impact broken samples and to establish the dispersion characteristics of hybrid composites. The observed microscopic images revealed a good dispersion of clay particles at low clay loading (Fig. 10(B), and 10(C)) and agglomeration build up at higher clay loading (Fig.

10(D), 10(E) and 10(F)). In flake like structure of neat epoxy reveals the brittleness. This has been reduced as the reinforcement is increased. At low clay loading fiber pullout is more. Fiber pullout and fiber de-bonding contributes largely to the dissipation of energy during fracture and increases the impact strength (Debdatta Ratna 2005). When clay is increased beyond 0.5 phr the fiber pullout is decreased, reducing the impact strength. Also clay particle agglomeration can be found in higher clay loaded sample. These agglomerations act as stress concentrators which have decreased the strength between the matrix and the fiber resulting in the initiation of cracks.

4. Conclusions

Composite hybrids were prepared using epoxy as a matrix, polypropylene short fibers and clay particles as reinforcements. The tensile, impact, thermal and flame retardancy behaviors of the composite hybrids with different PP short fibers and 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 hybrids increased with the increase of both reinforcements. However, these properties decreased as the reinforcements load was raised beyond 0.5 phr each. The elongation at break was found to decrease. Thermal stability of the material was found to increase with the increase in reinforcements up to 0.2 phr each, beyond which it is decreased. The improvement in mechanical and thermal properties at lower reinforcement load is attributed to the dispersion of clay and short fibers throughout the matrix. The clay particles at lower load has avoided bunching of short fibers, in turn, contributed to the increase of mechanical properties. The short fibers dissipate energy efficiently and increase the mechanical performance of composite hybrids. At higher loads, the clay particles agglomerate and are incapable of avoiding bunching of fibers and act as stress concentrators leading to decrease the mechanical performance of composite hybrids. The increased thermal stability of the composite system is due to the better dispersion of clay and PP short fiber in the matrix and good adhesion between PP short fiber and epoxy promoted by clay at lower clay loading. This has hindered the heat propagation, thereby reducing the degradation rate. Adhesion between epoxy and PP short fibers has restricted segmental motion resulting in increase of thermal stability. The decreased activation energy at higher clay load is 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 clay particles, which thermally insulate and produce low permeable char residue on clay layers at the outer surface of the composite during combustion and act as barriers by reducing heat and mass transfer between the flame and matrix. The char residue of clay will reduce the oxygen uptake and the escape of volatile gases produced by polymer degradation. Also the tortuous paths created by clay galleries have retarded the burning rate by retarding the diffusion of gas molecules through the polymer matrix. To find the synergistic effect of PP short fiber and clay particles, epoxy-0.5 phr PP short fiber sample was prepared and characterized. The addition of clay particles has adversely affected the mechanical performance of epoxy-PP short fiber composite. The morphology of impact broken samples indicates better dispersion of clay particles and short fiber at lower load. It shows a decreased flaking with a higher reinforcement load that has led to the increase in ductility. Also the reduced fiber pullout at higher load indicates decrease in the mechanical performance of composite hybrids.

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