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Effect of Montmorillonite Clay Content on the Mechanical and Thermal Properties of Flame Retardant Epoxy Nanocomposites

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ABSTRACT

In the present investigation an effort has been made to develop nanocomposites using epoxy resin as polymer matrix and MMT as reinforcing agent. This study has been conducted because flame-retardant epoxy resin has wide applications in adhesive, coatings and as advanced composites in the aerospace and electronic industries. Nanocomposites have been prepared through melt mixing process. Mechanical Properties of the developed nanocomposites have been evaluated by universal testing machine. Thermal stability has been studied by thermo-gravimetric analyzer. TGA results revealed that there is appreciable improvement in thermal stability due to increase of MMT content in the epoxy resin. It has been also been observed that maximum thermal stability has been achieved with 3 wt % content of MMT in epoxy resin. It has been observed that the limiting oxygen index values has shown remarkable improvement in flame retardant characteristics of the developed nanocomposites. The structure-Property relationship has been established with the help of FTIR. The distribution pattern of the MMT in the epoxy matrix has been studied through XRD. Morphological studies of the developed nanocomposites have been characterised with the aid of scanning electron microscope (SEM). It has been observed that there is excellent improvement in mechanical properties, thermal stability and flame retardant properties due to incorporation of MMT in epoxy matrix.

Keywords - Epoxy, MMT, Thermal Stability, SEM, Mechanical Property.

I. INTRODUCTION

Now a day's epoxy resins are thought to be an important class of thermo-setting polymers, which are extensively used as materials for the development of composites and structural adhesives [1-5]. It is very well cited in the literature that pure epoxy resin is a cross-linked network which has extremely high modulus and fracture strength, low creep and excellent performance at elevated temperature owing to this reason they are extensively used in various fields of engineering. To name a few of them are electrical industry and for structural application in both civil and military aircraft industry. Truly speaking, they lack in adequate thermal and mechanical properties. In view of the above fact, it is mandatory to modify epoxy resin using appropriate modifier and nanoclay.

In the present scenario flame retardant epoxy resins have high demands because they have pronounced applications in the aerospace and electronic Industries [6,7]. The valuable way to improve flame retardant in epoxy resin is to incorporate zinc borate, Sb_2O_3, phosphorus etc into polymer backbone or side chain. It has also been observed that incorporation of sulphone into the epoxy matrix provides the resin transparency which is useful for exposure to water and chemicals. It enhances the resistance of the resin to thermal oxidation and can also provide easy processing [8].

Earlier researchers have shown in their studies that the introduction of siloxane in epoxy resin may provide appreciable enhancement in various properties such as mechanical properties, anti corrosive characteristics and thermal stability. The incorporation of siloxane in epoxy resin also helps in good processability, flexibility, toughness, chemical and weather resistance along with thermo-oxidative stability. Thermo-oxidative stability may be attributed to the high bond dissociation energy of Si-O unit bond as compared to C-O [9-12].

In the present era, fillers with a high aspect ratio have been thought to be good candidates for flame retardant additives. Because of this reason, they have been used as flame retardant fillers. They can promote formation of standard network, resulting in improving the mechanical properties of polymer matrix [13-15]. MMT is frequently used as nano-filler in polymer composites. It can act as barrier to oxygen and flammable material [16, 17].

At present MMT and CNTs are extensively applied as nano-fillers because they help in improving the flame retardant and mechanical properties of epoxy resin [18-20]. The present studies have been conducted to investigate the ability of MMT to provide the epoxy resin with improved flame retardant and thermally resistant properties. The developed nano composites have been characterized by various advanced analytical techniques such as TGA, UTM, SEM etc.

II. EXPERIMENTAL

Materials

Diglycidylether of bisphenol A (DGEBA) (LY-556) [Ciba Geigy India Ltd] has been used as the epoxy resin. Triethylenetetramine (TETA) (HY-951) is used as the curing agent.

AR grade zinc borate has been used as a flame retardant additive. Its concentration has been taken as 30 wt % in fabrication of the flame retardant nanocomposites.

Preparation of Nanocomposites

Epoxy resin has been heated at 80°C for 5 minutes. Organically modified MMT has been incorporated in the epoxy matrix at various loadings viz. (0,1,2,3,4,5) Wt. % and then manually stirred for 1 hr. The composite sheet of all compositions have been prepared at room temperature under a load of about 80 kg for 24 hrs in hydraulic compression moulding machine, and at that stage hardener is mixed in a ratio of 10:1 by weight. Obtained sheets have been post cured at 60°C for another 24 hrs after removing out from the mould. Then, the specimens of suitable dimension have been cut from the sheets using a cutter for mechanical testing and various characterizations. Composites formulations are given in Table 1.

Table 1 : Composites Formulations

Sample Codes	Epoxy Resin (Gm.)	Zinc Borrate (Zb) (Wt. %)	Organically Modified MMT (Wt. %)
M_0	100	0	0
M_z	100	30	0
M_1	100	30	1
M_2	100	30	2
M_3	100	30	3
M_4	100	30	4
M_5	100	30	5

III. TESTING & CHARACTERIZATION

Mechanical Properties

Mechanical properties such as tensile strength, tensile modulus, flexural strength and flexural modulus of the developed nanocomposites have been determined with the help of Universal Testing machine (Instron 3382) using 10 KN load cell at the speed of 5 mm/min as per ASTMD 638 and ASTMD 790 test methods respectively.

Thermal Properties

Thermal stability of the developed nanocomposites has been evaluated with the aid of thermo gravimetric analyzer (Perking-Elmer Pyris TGA) in the temperature range of 50-7500C under a constant heating rate of 100C/min in nitrogen atmosphere.

Morphological Studies

Morphological studies of the developed nanocomposites have been carried out with the help of scanning electron microscope (SEM) [Model JCM 7000, Jeol, Japan]. Prior to SEM analysis specimens have been gold coated with help of gold sputtering unit just to avoid charging effect and to enhance the emission of secondary electrons.

Flame Retardant Test

The flame retardant test of all the developed nanocomposites have been conducted by measurement of limiting oxygen index (LOI) value by a Flammability Tester [Model Red Craft UK] as per the ASTMD 2863-77 for self supported samples.

IV. RESULTS AND DISCUSSION

Mechanical Properties

Mechanical properties results are depicted in Table 2 for pure epoxy and developed nanocomposites. It is obvious from table that the nanocomposites having 3 wt% MMT content shows highest mechanical properties that can be attributed to that there may be physisorption of the polymer chains on the silicate surface that stiffened the nanocomposites. Thus, the applied load to the polymer is transferred to the clay. Obviously for such high aspect ratio nano-filler (MMT), the surface area exposed to the polymer is large and therefore, the tensile strength increases remarkably at 3 wt% filler content.

Flexural modulus and strength results for the epoxy and developed nanocomposites are given in Table 2. It can be observed that the addition of MMT increases the modulus of developed nanocomposites by 4 %. This is thought to be assisted by the rule of mixture theorem, which states that the addition of micro and nano particles offer greater stiffness than the epoxy matrix [21,22]. From the Table 2, it is also evident that the flexural modulus values almost remain constant for all nanocomposites, with the main exception of the nanocomposites having 4 wt. % of nanoclay. This reduction may be attributed to smaller aggregates and disordered nature of the clay. It is very well documented in the open literature that when platelets are ordered, their anisotropic behaviour can render higher stiffness when aligned in the direction of strain. Therefore, a disordered morphology may have the opposite effect. Truly speaking, it appears that the modulus effect differs when the particle size changes. It is also demonstrated [23] that there is a critical particle size that alters the nanocomposites modulus, which in our studies takes place for the nanocomposites having the 4 wt.% of MMT. Flexural strength can be influenced by the void content, clay dispersion, interfacial interaction between clay & epoxy and structure of materials.

Sample Codes	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
M0	35.85	1145.6	3.30	68.87	2170.8
M1	36.16	1195.5	3.37	68.96	3787.0
M2	38.92	1210.6	3.67	69.17	3884.0
M3	40.63	1374.8	4.14	71.72	3991.9
M4	38.77	1224.7	3.67	70.02	3242.7
M5	37.84	1184.6	3.49	69.72	3660.2

Thermal Properties

The TGA thermo-grams of pure epoxy and nanocomposites with various loadings of MMT are depicted in Figure 1 and Table 3.

Table 3 : Thermal stability results

Sample Code	Onset Temperature (⁰C)	Final Temperature (⁰C)	Residue (wt %) at 700⁰C
M0	250.16	663.96	8.132
M1	220.36	662.29	28.124
M2	231.78	666.89	29.161
M3	285.34	697.00	27.479
M4	208.79	661.03	30.207
M5	215.43	670.15	29.488
ZB	196.62	686.95	25.643

It can be seen that the initial decomposition of pure epoxy take place at 250⁰C while for nanocomposites, decomposition occurs at 220, 231, 215, 208, and 285⁰C for various loadings of MMT respectively. However, the stability upto 250⁰C for pure epoxy can be explained from the cross-linking between the free hydroxyl group, which may be present in the fatty acids or generated during the amine cross-linking reaction as well as good chemical interactions via hydrogen bonding and polar-polar interactions. Appreciable enhancement in the thermal stability of nanocoposites has been observed. The increase in onset degradation temperature upto 35⁰C has been achieved for nanocomposites. The increase in initial decomposition temperature for nanocomposites may be because of the protection of polymer chains that are present between the nanoclay layers. The network of polymer chains present between the nanoclay layers are confined due to restricted segmental motion, which results in higher thermal stability than the pure system. Inorganic compounds like oxides of silicon, aluminium and magnesium that are formed in the nanocomposites are responsible for enhancement in thermal stability of the developed nanocomposites. The formation of char after thermal decomposition may also enhance the thermal stability of the developed nanocomposites [24]. It is also evident that the nanocomposites comprising of 3 wt % loading of modified MMT has the highest thermal stability because this particular nano composites has minimum weight loss.

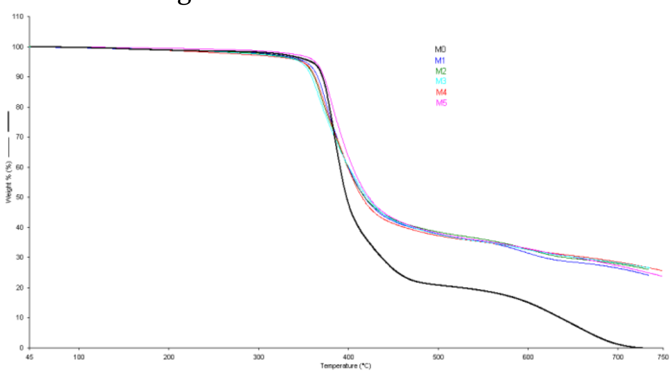

Figure 1. TGA thermo-grams of epoxy nanocomposites with different loadings of MMT.

Morphology of nanocomposites

(Figure 2 a – c) depicts the SEM micrographs of the surfaces corresponding virgin epoxy (M_0), Epoxy with zinc borate (Zb) and Epoxy/ZB/MMT (M1) nanocomposites. It is observed that the surface of the pure epoxy is smooth. This indicates that some amount of toughness has been induced in the resin due to the incorporation of organoclay[25]. It is evident from SEM micrographs that there is uniform and homogeneous distribution of nano-filler over the entire polymer matrix. SEM micrograph for nanocomposite having 3 wt % MMT has excellent dispersion of nano-filler over the entire polymer matrix. Because of this reason, almost all the properties relating to mechanical and thermal have improved significantly.

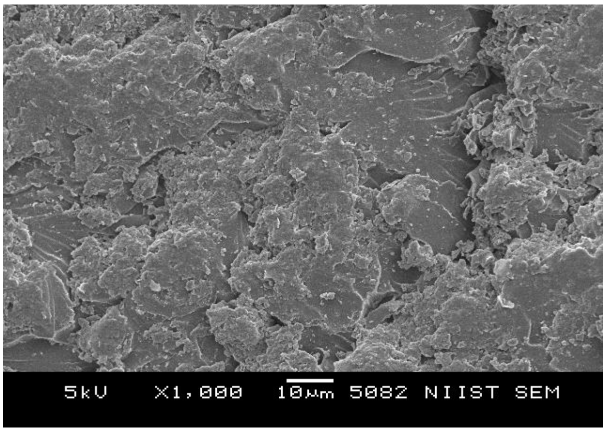

Figure 2-a

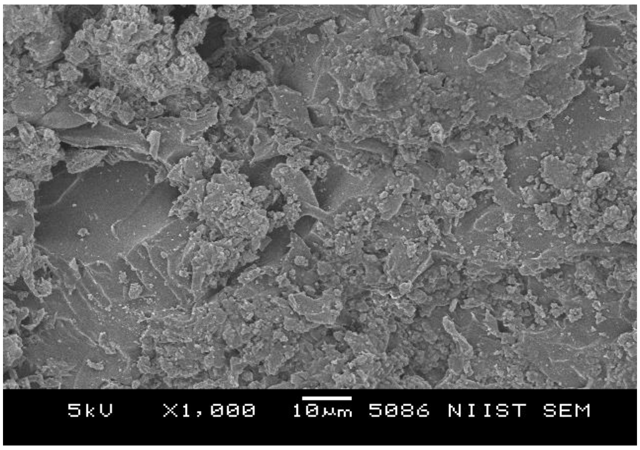

Figure 2-b

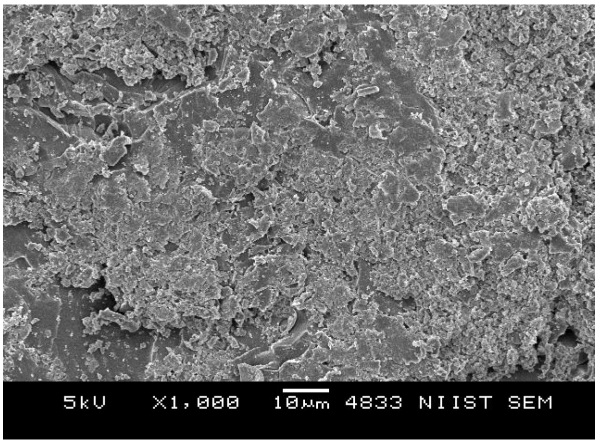

Figure 2-c

Flame Retardancy

The LOI representing the lowest oxygen volume content for sustaining the flame in an environment, has been used for quantifying the flame retardancy of epoxy resin. The oxygen volume content in ambient atmosphere is about 21%. Therefore, a material exhibiting its LOI above 21 might show flame retardant property. Generally, materials with LOI values higher than 26 might show self extinguishing behaviour and is considered to be highly flame retardant. The result of LOI for epoxy resin and its composites are listed in Table 4.

Table 4 : Limiting Oxygen Index (LOI)

Sample Code	LOI %
M0	17.2
M1	18.3
M2	20.6
M3	22.3
M4	28.4
M5	20.8
ZB	19.0

The LOI of the developed nanocomposite has been investigated to find out the essential oxygen content for ignition. It is obvious from Table 4, that LOI increases from 17.2 to 28.4 % due to the effect of additives. Thus, the essential oxygen content for ignition increases, making it very difficult to ignite the complex of additives and epoxy resin. The structure network layering by MMT plays an important role as a shield and re-emitted much of the incident radiation back into gases, lowering down the rate of polymer degradation [26, 27].

MMT inside the epoxy resin also plays an important role in flame retardant properties. The main role of MMTs can be understood in two ways. Firstly, MMT has high aspect ratio around few thousands, secondly, MMT has a high specific heat: thus, MMT can act as a heat storage medium. During combustion of the complex, the applied thermo-energy can be stored in MMT and hinder the spread of thermal energy to the epoxy resin.

V. CONCLUSION

Flame retardant epoxy resin nanocomposites reinforced with MMT at various loadings having 30 wt% zinc borate flame retardant additive, has been prepared with the help of compression moulding technique. It has been observed that the mechanical properties, thermal stability and flame retardant properties has remarkable enhancement due to incorporation of MMT in polymer matrix. Maximum enhancement in various properties of developed nanocomposites have been achieved at 3 wt% MMT content in epoxy matrix. Morphological studies as studied by SEM reveal that MMT has an excellent dispersion for the nanocomposites having 3 wt% content of MMT over the entire epoxy matrix surface. These developed nanocomposites have variable applications in aerospace industry.

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