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INVESTIGATION ON THERMAL, MECHANICAL AND MORPHOLOGICAL BEHAVIOURS OF ORGANO NANOCLAY INCORPORATED EPOXY NANOCOMPOSITES

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ABSTRACT

A series of epoxy nanocomposites have been prepared with varying compositions viz., 0, 1, 3, and 5 wt % organically modified montmorillonite (MMT) clay. The effects of MMT nanoclay content on the physico-mechanical and thermal properties of epoxy nanocomposites have been studied. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been employed to investigate the thermal characteristics and their mode of thermal degradation. The TGA thermograms of nanocomposites exhibits higher decomposition temperature behaviours compared to the pristine epoxy. It was found that the thermal degradation of all epoxy nanocomposites takes place in one step. All the nanocompsoites were stable upto 221 °C. The thermal degradation kinetic parameters of the composites have been calculated using two mathematical models namely, Coats-Redfern and Broido's methods. The rheology of polymer was envisaged by DMA is affected on the polymer nanocomposite. Morphological behavioours of epoxy/o-MMT nanocomposites assessed by scanning electron microscopy (SEM) method.

Keywords: epoxy, organo clay, nanocomposite, mechanical properties, thermal behaviour, thermal degradation, kinetic parameters.

1. INTRODUCTION

As widely used thermosetting polymers, epoxy resins have several unique characteristics, high adhesive strength, high strength and hardness, excellent chemical and heat resistance. Epoxies have been widely used in various industrial applications, particularly as adhesives for bonding and as matrix resins for producing high-performance fibre reinforced composites.

However, most cured epoxy systems exhibits low fracture toughness, poor resistance to crack initiation and propagation, and inferior impact strength. For example, delamination and poor impact resistance of fibre reinforced epoxy composites is often attributed to the low fracture toughness of epoxy matrix. Many efforts have been made in the past decades to improve the fracture toughness of epoxies by modifying epoxy resins with additives such as rubbers, thermoplastics, and inorganic particles (1-2). Inorganic additives, such as silica, alumina and glass particles, have been found in recent years to be more promising modifiers for increasing the mechanical performances of epoxies without sacrificing their basic properties (3-4). More recently there has emerged a new technology based on the formation of a nano-phase structure, consisting of small rigid particles or fibres with a diameter (or at least one dimension) of less than 100 nm dispersed in epoxy matrices, which holds a great promise for increasing the mechanical performance of epoxies without compromising other desirable mechanical and thermal properties of the modified systems. Due to the nanoscale dispersion and the high aspect ratios of the inorganic clays, polymer-layered silicate nanocomposites (PLSNs) exhibit light weight, good dimensional stability, high heat resistance, high stiffness, high barrier properties, and improved toughness and strength with far less reinforcement loading than conventional microcomposite counterparts (5-6). The interest in clay-polymer nanocomposites has been increasing ever since Toyota demonstrated commercial applications of nylon 6/clay nanocomposites (7).

In recent years the concept of forming hybrids using polymers and inorganic materials has received a significant amount of attention. Many of the researchers have used surface-treated silicates, or organoclays, to produce layered-silicate nano-composites (8-9). Many claims for the potential of these organic/inorganic hybrids have been made, but for some important combinations of materials little experimental data has been produced. Other types of nanoparticles are also being incorporated into polymeric resins in order to fabricate materials with increased performance. Some common examples of the nanoparticulate reinforcements include carbon-based nanoparticles such as nanotubes, metals such as copper and aluminum, and ceramics such as alumina and silica. These nanoparticles are loaded into epoxies, polymethyl methacrylate (PMMA), nylon, and polystyrene (PS), as well as other types of polymers. In some cases the nanoparticle-reinforced resins have been used as matrix materials to fabricate conventional microcomposites (10-11). Clay-epoxy nanocomposites have attracted considerable technological and scientific attention because these materials offer a wide array of property improvements at very low filler content. The effects of organoclay on modulus of elasticity (12), fracture toughness (13), tensile strength (14), and impact strength (15) of epoxy resins were investigated. In these invistigations, increasing of the modulus of elasticity and toughness, both increasing and decreasing of the tensile and impact strengths with increasing clay loading have been reported. Zilg *et al.* (13) proposed that intercalated

morphology improves toughness and formation of exfoliated morphology enhances the composite's stiffness. Montmorillonite (MMT) clay has a layered structure in which individual layers of typically 1 nm thickness and 0.1-2 µm length and width has interlayer spacing of 2-3 nm. These layers are bonded together by vander Waal's forces. The enhancement of mechanical properties in nanocomposites depends on the intercalated or exfoliated content of nanoclay in the polymer matrix. In the exfoliated condition their surface area can be as high as 750 m^2/g. However, the complete exfoliation of nanoclay remains a significant challenge in various types of polymers.

Considerable efforts have been made to study the thermal characteristics of nanocomposites using thermogravimetric analysis (TGA), because it analyzes the degradation response and determines the upper temperature limit of use and durability. Brown *et al* (16), and Feng *et al* (17) studied the T_g of epoxy/organoclay nanocomposites using dynamic mechanical analysis (DMA).

The present research article deals with the mechanical and thermal characteristics of epoxy/organo clay (MMT) nanocomposites. The thermal degradation kinetic parameters such of as activation energy (E_a) was calculated for the nanocomposites using two mathematical models namely; Coats-Redfern (18) and Broido's (19) methods and the results are compared.

MATERIALS AND METHODS

2.1 Materials

The bisphenol A based epoxy resin Araldite LY 556, is a clear liquid with a viscosity of 9000 to 12000 mPa at 25 °C and Hardener LY - 951, is a clear liquid with a viscosity of 5000 to 11000 mPa at 25 °C, were obtained from Huntsman Advanced Materials, Bangalore, India. The nanoclay used was organically modified montmorillonite (Nanomer 1.31PS) supplied by Nanocor, Inc., USA. This MMT nanoclay is surface modified MMT clay: (Na)-modifiers-gamma-aminopropyl triethoxysilane octadecylamine; and CEC is ~145 meq/100 g. The surface treatment of MMT is due to make it suitable for dispersion in an amine cured epoxy resin. All other chemicals used in this study are of AR grades.

2.2 Fabrication of Composites

Organoclay and epoxy resin were predried for about 2 h before use. As the MMT particles are formed in-situ during a sol-gel process, they have a narrow range of particle-size distribution and excellent dispersion in the host epoxy. Different amounts viz., 0, 1, 3 and 5 wt. % of organo MMT were mixed with the epoxy by means of a mechanical mixer stirring for 30 min at room temperature to obtain a homogenous mixture. The mixture was then degassed under vacuum for about 2 h. Upon completion of degassing, the vacuum was released and LY - 951 hardener was added at a ratio of 100:10 by weight while stirring slowly. The liquid mixture was then cast in preheated cleaned, releasing agent smeared moulds and cured at room temperature for 24 h. To ensure complete curing, the composite and matrix sheets were post cured at 140°C for 4 h. The post cured epoxy plates were left in the oven and allowed to cool gradually to ambient temperature before removal from the moulds. The cured epoxy laminates were machined into different test specimens for characterization.

2.3 Techniques

2.3.1 Physico -mechanical properties

The density of epoxy-clay nanocomposites were measured using Mettler electronic balance (Switzerland), Model AG 204 according to ASTM D 792-86. Hand operated durometer was used to measure the surface hardness (Shore D) of the nanocomposites according to ASTM D785. Tensile tests were carried out with an Instron 8511 universal testing machine under a strain rate of 5 mm/min at 25°C. All test specimens were made according to ASTM D 638-01. Minimum five samples were tested at room temperature for each formulation and an average values are reported.

2.3.2 Heat ageing

The heat ageing test has been carried out as per ASTM D3045 method. The specimens for heat aging were kept in conventional hot air oven at temperatures 250°C and 300°C. The annealing time began at the time of the specimens were placed in the oven and allowed for 1 h. The influences of heat aging on the change in colour and change in weight of the composites have been recorded.

2.3.3 Water uptake behaviour

Water absorption test was carried out according to ASTM D570-98. The dimensions of the specimens were 25 mm x 25 mm x 3.2 mm. Two specimens were tested for each analysis and an average value was reported. The water content of each sample was calculated by the following equation;

$$\text{Water uptake (\%)} = ((M_t - M_0)/M_0) \times 100 \quad (1)$$

Where, M_0 and M_t are the initial sample weight and the sample weight on the t-th days, respectively.

2.3.4 Chemical resistance

The chemical resistance of the composites was studied as per ASTM D 543.06 method. For this purpose different chemical reagents such as 10 % HCl, 10 % NaOH, 10 % H_2SO_4, 10 % Na_2CO_3, 10 % NH_4OH, hexane, benzene and water were used.

2.3.5 Thermal behaviour

The transition temperature of the specimens was examined by using differential scanning calorimeter (DSC) (model DSC-Q 200, USA) of DuPont TA instrument. All samples were sealed in hermetic aluminum pans. The mass of the sample used for analysis is in the range 8-10 mg. The thermal behaviours of the samples

were investigated at the heating rate of 5 °C/min from ambient to 300 °C under nitrogen gas flow of 60 mL/min. The thermal stability of the epoxy nanocomposites have been evaluated using DuPont TA instrument with TGA-Q 50 module. The instrument was calibrated using pure calcium oxalate sample before analysis. About 8-10 mg of sample was subjected to dynamic TGA scans at a heating rate of 20 °C/min in the temperature range of ambient to 700 °C in N_2 atmosphere. The TG curves were analysed as percentage weight loss as a function of temperature. The oxidation index (OI) was calculated based on the weight of carbonaceous char (CR) as related by the empirical equation;

$$OI \times 100 = 17.4 \times 0.4CR \quad (2)$$

From TGA curves thermal degradation kinetic parameters were determined for epoxy/MMT nanocomposites using Coats-Redfern (18) and Broido's (19) methods which provide overall kinetic data. Coats-Redfern (CR) (18) relation used to evaluate the degradation kinetic is;

$$\log(-\log(1-\alpha)/T^2) = (\log(AR/\beta E_a)) - (E_a/2.303RT) \quad (3)$$

where, α is the fraction of sample decomposed at time T, T is the derivative peak temperature, A is the frequency factor, β is the heating rate, E_a is the activation energy, and R is the gas constant.
A plot of log $\{-\log(1-\alpha)/T^2\}$ versus 1/T gives the slope for evaluation of the activation energy most appropriately. Mathematical expression of Broido's (BR) (19) method is as follows;

$$\text{Log}(-\log(1-\alpha)) = -(E_a/2.303R)((1/T) + K) \quad (4)$$

where, (1-α) is the fraction of number of initial molecules not yet decomposed, T is the peak temperature of derivative curve of TGA, R is the gas constant and E_a is the activation energy can be calculated from the plot of log $\{-\log(1-\alpha)\}$ versus 1/T.

The storage modulus (E') and the mechanical loss factor ($\tan\delta = E''/E'$) as a function of temperature (T), were assessed by dynamic mechanical thermal analysis (DMA) using a DuPont TA instrument, USA, with model 2980-DMA. DMA thermograms were recorded in tension mode at 5 Hz frequency and at a heating rate of 3°C/min in the temperature range 30 - 160 °C.

The scanning electron microscope (SEM) (Hitachi S-2150) was used to study the microphase separation of the nanocomposites. The tensile fractured samples were used for SEM studies. The fracture samples were glued on the aluminum sample holders and gold coated before analysis.

3. RESULTS AND DISCUSSIONS

3.1 Physico-mechanical properties

The measured physico-mechanical properties of the epoxy/organoclay nanocomposites are tabulated in Table-1. The presence of voids has a deleterious effect on the mechanical properties of the composite. Hence, density measurements were performed on all nanocomposites to ensure void free composites. As expected, the nanocomposite density increased as increase in nanoclay content. From Table-1 it was noticed that neat epoxy resin cast had an average density of 1.18 g/cc. After incorporating nanoclay, a slight increase in the density of the composite was observed as compared to neat epoxy system. This increase in density of the composites is attributed to the incorporation of high dense filler (2.53 g/cc) in low dense epoxy matrix. The density values of the composites lie in the range 1.122 - 1.178 g/cc. The theoretical density was calculated for composites by weight additive principle, which states that;

$$d = w_1 d_1 + w_2 d_2 \quad (5)$$

Where, d is the density of the composite, w_1 and w_2 are the weight fractions of the constituents and d_1 and d_2 are the corresponding densities.

The theoretically calculated density values are higher as compared to corresponding experimentally obtained values (Table-1). This may be due to void formation and poor interfacial adhesion between epoxy matrix and filler in the composites. The density of neat epoxy (1.122 g/cc) increased by 1.78 % upon the addition of 5 wt. % of organo nanoclay.

Surface hardness is a measure of resistance to indentation. Surface hardness indicates the degree of compatibility and crosslink density. The surface hardness of the nanocomposites increases as increase in clay content. The reason for the improvement in the hardness is due to the presence of intercalated and exfoliated clay platelets in the base matrix. The intercalated/exfoliated clay platelets effectively restrict indentation and increase the hardness of the nanocomposites (20).

It has been found that, incorporation of o-MMT has increased the tensile strength, percentage of elongation at break and tensile modulus of the composites (Table-1). Tensile strength of MMT filled epoxy significantly enhanced from 39 MPa to 68.6 MPa marked improvement in percentage elongation at break from 3.2 to 6.2 and tensile modulus slightly increases from 11.02 to 12.95 GPa on increasing the organically modified MMT content in epoxy matrix from 0 to 5 wt %. From the calculated tensile modulus data it was found that the modulus was increased around 12 and 18 % for 3 and 5 wt. % of MMT loaded nanocomposites respectively. The ensured modulus was found to increase with an increasing proportion of MMT. The observed result reveals that, the tensile behaviours depend on filler content.

3.2 Effect of heat ageing

Plastic materials exposed to heat may be subjected to many types of physical and chemical changes. The severity of the exposures, both time and temperature determines the extent and type of changes that take place. Extended periods of exposure of plastics to elevated temperature will generally cause some degradation with progressive changes in physical properties. Hence, epoxy/organoclay nanocomposites were subjected to heat

ageing at two temperatures viz., 250, and 300 ^{o}C for 1 h and the change in weight was monitored. The measured weight loss at both temperatures for all nanocomposites is given in Table-2. The higher weight loss in case of nanocomposites as compared to pristine epoxy is due to, the presence of organic component in the modified MMT, which degrades under the studied condition. From the heat aging test it was observed that there was a slightly reduction in thermal stability of the composites after incorporation of MMT. However, there was no considerable weight loss of nanocomposites upto 250°C. Hence, epoxy nanocomposites may be safely used upto 250°C.

3.3 Water uptake behaviour

The plot of water uptake as a function of duration of exposure for epoxy nancomposites are shown in Figure-1. From the Figure it was noticed that lower water uptake behaviour for composites as compared to neat epoxy. This result indicates that nanocomposites are resistive to water. However, a slight increase in water uptake behaviour with duration of exposure was noticed. Furthermore, as increase in MMT content in epoxy matrix, the composites becoming more resistive towards water.

3.4 Chemical resistance

The nanocomposite specimens were exposed to different chemical environments in order to investigate the effect of these chemical environments on the nanocomposites. An excellent chemical resistance was shown by all the epoxy/o-MMT nanocomposites for all chemical reagents under investigated different (Table-3). This may be due to compact three dimensional crosslinked structures of the epoxy nanocomposites, and longer diffusion path of the systems.

3.5 Thermal behaviour

Figure-2 shows the dynamic DSC thermograms for neat epoxy and their nanocomposites with different contents of organo modified MMT (0, 1, 3 and 5 wt %). The T_g values of composite lies in the range 62.5 - 76.5°C. The DSC thermograms have been shown that T_g was reduces after incorporation of nanoclay in epoxy matrix (Table-2). This can be attributed that, the presence of organic component in the modified MMT, which acts as plasticizers. Similar kind of observation was made by several researchers (21-22). Xu *et al* (21) measured T_g of epoxy/o-MMT nanocomposites using dynamic mechanical thermal analysis (DMTA) and they also observed that the reduction in T_g with increase in clay content in epoxy matrix. They thought this T_g reduction might be associated with the void of crosslinking in the composites, because the organoclay could change the chemistry of the curing reaction. Zilg *et al* also made similar kind of observation for epoxy nanocomposites [22].

The TGA thermograms of epoxy and 3 % nanoclay loaded epoxy composite are shown in Figure-3 (a)-(b) respectively along with derivative thermograms. TGA thermograms of all epoxy nanocomposites are shown in Figure-4. The temperature range of thermal degradation was analyzed from the TGA thermograms and is given in Table-4. TGA thermogrmas of pristine epoxy and its nanocomposites indicate one stage thermal degradation process. The thermal degradation of neat epoxy occurred in the temperature range 211-470°C with the major weight loss of around 99.7 %. The decomposition temperature of nanocomposites was started at 221°C and takes place up to 505°C, which corresponds to the weight loss ranging from 93.9 to 89.3 %. It was found that the pure epoxy degrades slightly faster than the nanocomposites. The onset degradation of epoxy/o-MMT nanocomposites is slightly higher than that of neat epoxy (Table- 5). This can be attributed to the presence of MMT, which has relatively higher thermal stability than epoxy. The obtained percentage ash content is higher in composites as compared to neat epoxy (0.3 %). The ash content of epoxy nanocomposites increases with increase in nanoclay content as expected and it lies in the range 6.1-10.7. This is slightly higher than the actual nanoclay loaded to epoxy system. This is due to the TGA studies conducted in an inert gas media. From TGA curves it can be clearly observed that the weight loss markedly decreases with increase in NC content.

Some characteristics TGA data related to the temperature corresponding to weight loss such as T_0 (temperature of onset decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{50} (temperature for 50 % weight loss) and T_{max} (temperature for maximum weight loss) are the main criteria to indicate their thermal stability of the composites. The relative thermal stability of epoxy nanocomposites have been evaluated by comparing the decomposition temperatures at different percentage weight loss (Table-5). Higher the values of T_{10}, T_{20}, T_{50} and T_{max} higher will be the thermal stability of the composites (23).

Figure-3 and Table-4 data reveals that the initial stages thermal degradation process pattern is almost same for both unfilled and nanoclay filled epoxy composites. Hence at the tired stapes marked improvement in thermal stability for nanocomposites than epoxy was noticed. This can be attributed to the synergistic effect of MMT and matrix present in the composite. Higher the values of oxidation index (OI), higher will be the thermal stability (23-24). From the Table it was observed that the oxidation index values increases noticed with increase in o-MMT content and it lies in the range 0.02-0.74. This data indicates that the o-MMT filled epoxy composites were more thermally stable than that of pristine epoxy. Annakutty *et al* reported that, the char yield is directly correlated to the potency of flame retardation [25]. From the aforesaid investigation, it can be concluded that the flame resistance of nanocomposites was increased as increase in MMT content.

Kinetic analysis of thermal degradation

Kinetic parameters were evaluated from TGA curves using Coats-Redfern and Broido's methods. The

plots of ln [-ln (1-α)]/T^2] versus 1/T (CR) and ln [-ln (1-α)] versus 1/T (BR) for epoxy/o-MMT nanocomposites are shown in Figures 5 and 6 respectively. The regression analysis gives the slopes, constants and R^2 for degradation process. The linear plot with concurrency value (R^2) closer to one was chosen for both methods. The R^2 values and calculated activation energy (E_a) for thermal degradation process and for each method are tabulated in Table-6. The E_a values lies in the range 94.7 - 134.4 kJ/mol for Coats-Redfern and 105.8 – 145.5 kJ/mol for Broido's method. Lower E_a values were observed for nano filler loaded epoxy nanocomposites. This is due to after incorporation of MMT, formation of low molecular weight epoxy between interlayers of nanoclay, for which less energy is sufficient for degradation.

3.6 Dynamic mechanical analysis (DMA)

The effect of MMT reinforcement on storage modulus and Tan δ of epoxy/o-MMT nanocomposites can be seen from Table-7 in which we list the average values of the storage modulus (E') with different percentage weight of MMT. The E' of epoxy resin measured at 40 °C was 2.779 GPa and it decreases, for nanocomposites monotonically with the MMT content increase. The results obtained in this study are comparable to the literature data [26]. Table-7 also lists the average values of T_g for different wt. % of MMT. The measured T_g of epoxy resin was 91.1 °C. The effect of MMT loading on E' and T_g can be noticed in Figure-8, in which the addition of MMT did not significantly change the glass transition temperature of the epoxy resin, and it decreased by increasing nanoclay. For the addition of 3 wt. % MMT, the T_g of nanocomposite was 5° less than that of epoxy resin. MMT, when completely exfoliate and disperse, it is expected to increase the T_g of polymers by restricting the molecular mobility at higher temperatures. While some authors have reported an increase in T_g [27], others have reported decreased T_g [28]. The absence of entanglement surrounding the nanoclay, the effect due to surface modifiers, unreacted resin plasticization, and a lower cross-link density have been attributed to the decrease in T_g. Table-7 lists the average values of Tan δ for different percentage weight of MMT. It can be seen from Table-7, that Tan δ show no significant change by the addition of MMT. Various mechanisms like matrix viscoelasticity, filler/filler interfacial friction, etc., could increase the damping capacity of the polymer composite materials. However, the molecular motion at room temperature is frozen, and this may not contribute to the damping mechanisms. Table-7 lists the average values of Tan δ at T_t for different percentage weight of MMT. At T_t, the Tan δ value is higher for nanocomposites indicating the viscous damping because of the segmental motion in the polymer. Tan δ at T_t of the nanocomposites was in general higher than that of epoxy resin, and it increased as the percentage weight of MMT increased. Tan $_{max}$ δ at T_t for 5 wt. % MMT composites was about 4% higher than that of epoxy resin. This increase in the damping factor was attributed to the restriction to the molecular movements of MMT, which caused reduction in the matrix viscoelasticity. However, this did not improve the T_g, in our samples unlike others [27] who reported increase in the T_g of the nanocomposites. This is somewhat intriguing but literature reports are on both sides.

3.7 Scanning electron microscope (SEM)

The morphologies of epoxy/o-MMT nanocomposites were investigated by scanning electron microscopy (SEM). Figure-9 shows the SEM photo of epoxy-composites o-MMT content ranging from 1 to 5 wt. %. Figure-9 presents the fracture surface of 1% MMT composite, showing that MMT particles dispersed well within the polymeric matrix. MMT particles are of higher surface energy than polymers in the composites. Generally, when either a polymer melt or solution is placed on a substrate with higher surface energy, it will spread on the surface with high surface energy. Therefore, there exists adhesive interaction between nanoclay particles and polymer matrix. Composite with 1% MMT, It is evident that better interfacial adhesion between MMT particles and matrix was observed. The improved interfacial adhesion results in the enhanced mechanical properties of the composites. However, aggregation of fillers particles within composites 5 % wt. % can be seen in Figure-9.

Table-1. Phsico-mechanical properties of organoclay loaded epoxy nanocomposites.

MMT content in epoxy (wt %)	**Density** (g/cc)		**Tensile modulus** (GPa)	**Tensile strength** (MPa)	**Elongation at break** (%)	***Surface hardness***
	Expt.	**Theor.**				*(Shore D)*
0	1.122	-	11.02	39.0	3.2	*24*
1	1.077	1.189	11.89	41.6	3.4	*25*
3	1.145	1.216	12.34	61.4	5.4	*26*
5	*1.177*	*1.243*	*12.95*	*68.6*	*6.2*	*30*

Table-2. Percent weight loss of epoxy/o-MMT clay nanocomposites after heat ageing for 1 h at different temperatures.

MMT content in epoxy (wt %)	**Weight loss at different temperatures** (°C)		T_g (ºC)
	250 °C	300 °C	
0	0.70	1.67	76.5
1	0.82	1.83	62.5
3	0.89	2.32	63.6
5	0.84	1.99	66.2

Table-3. Chemical resistance of pristine epoxy and its nanocomposites.

MMT content in epoxy (wt. %)	**10 % HCl**	**10 % H_2SO_4**	**10 % NaOH**	**10 % Na_2CO_3**	**10 % NH_4OH**	**C_6H_6**	**C_6H_{14}**	**H_2O**
0	0.014	0.031	0.007	0.009	0.014	0.302	0.012	0.011
1	0.008	0.023	0.005	0.007	0.012	0.242	0.008	0.010
3	0.007	0.019	0.004	0.006	0.010	0.159	0.007	0.009
5	0.004	0.002	0.002	0.004	0.006	0.116	0.005	0.07

Table-4. Thermal degradation temperature range obtained from derivative TGA curves of epoxy/o-MMT nanocomposites.

MMT content in epoxy (wt. %)	**Temperature range** (˚C) **± 2**	**Ash content** (%)	**Oxidation index** (OI)
0	211 - 470	0.3	0.02
1	221 - 495	6.1	0.42
3	235 - 500	8.9	0.61
5	237 - 505	10.7	0.74

Table-5. Thermal data obtained from TGA thermograms of epoxy/MMT nanocomposites.

Clay content in epoxy (wt. %)	**Temperature at different weight loss** (± 2 ºC)				
	T_0	T_{10}	T_{20}	T_{50}	T_{max}
0	211	356	366	387	440
1	221	360	363	389	446
3	236	357	367	393	455
5	239	359	368	393	474

Table-6. Activation energies calculated by coats-redfern (CR) and broido´s (BR) methods with the respective concurrency value (R2) for epoxy/MMT nanocomposites.

MMT content in epoxy (wt. %)	**Activation energy** (E_a) (kJ/mol) **± 4** %			
	CR	**R^2**	**BR**	**R^2**
0	134.4	0.982	145.5	0.984
1	121.9	0.985	132.8	0.988
3	94.7	0.962	105.8	0.969
5	117.1	0.978	128.1	0.982

Table-7. Results of DMA analysis of epoxy /o-MMT nanocomposites.

MMT content in epoxy (wt. %)	**E'** (MPa) **at 40 ^{0}C**	**E"$_{max}$** (MPa)	**Tan$_{max}$ δ**	**Temperature** (^{0}C)	
				E"$_{max}$	**Tan$_{max}$ δ**
0	2779	401	0.87	77.8	91.1
1	2572	360	0.90	79	90.5
3	1896	270	0.80	75	85.5
5	1793	278	0.90	75	82.8

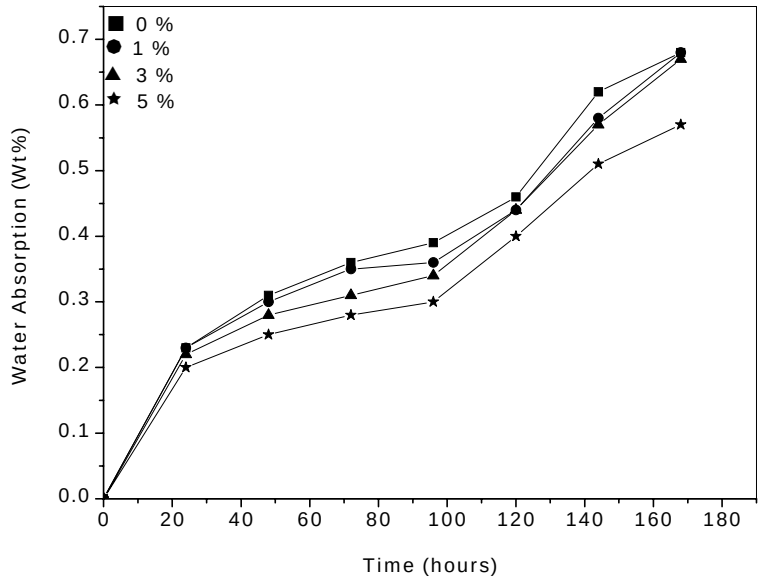

Figure-1. Water uptake behaviour of, 0 % MMT (■), 1 % MMT (●), 3 % MMT (▲) and 5 % MMT (★) incorporated nanocomposite when immersed in deionized water at room temperature.

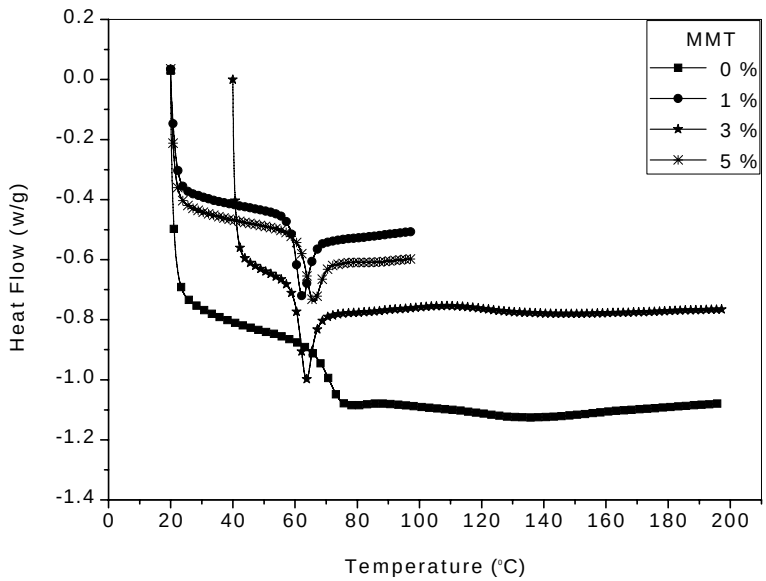

Figure-2. DSC thermograms of epoxy and their nanocomposites.

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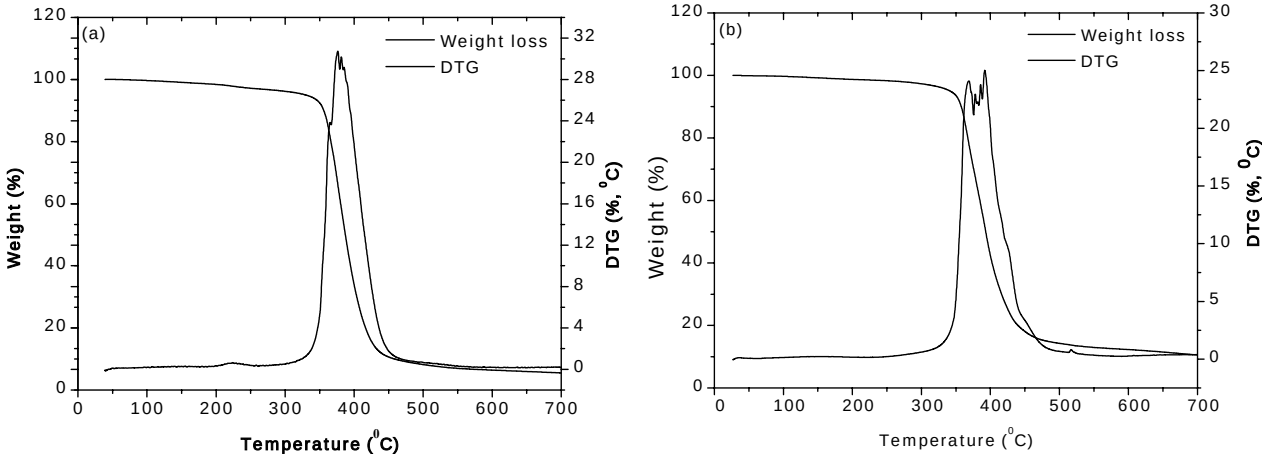

Figure-3. TGA and derivative thermograms of, (a) 0 % and (b) 3 % MMT filled epoxy nanocomposites.

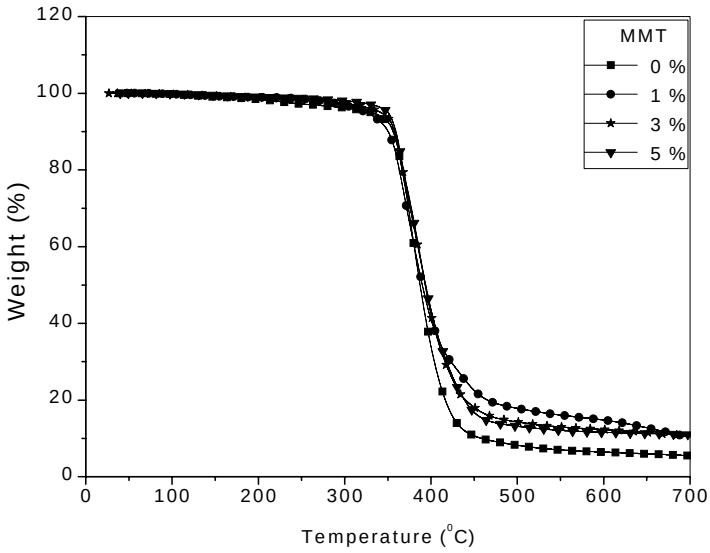

Figure-4. TGA thermograms of epoxy and its nanocomposites.

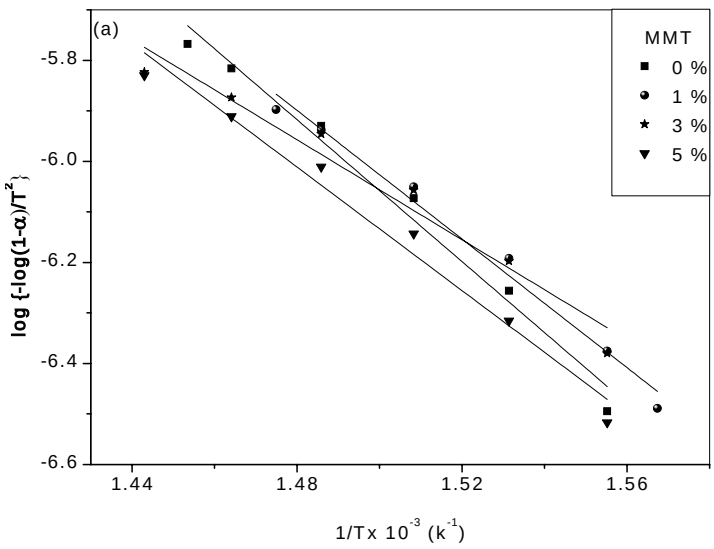

Figure-5. Plots of log {-log (1- α)/T^2} versus 1/T using coats-redfern method for epoxy/MMT nanocomposites.

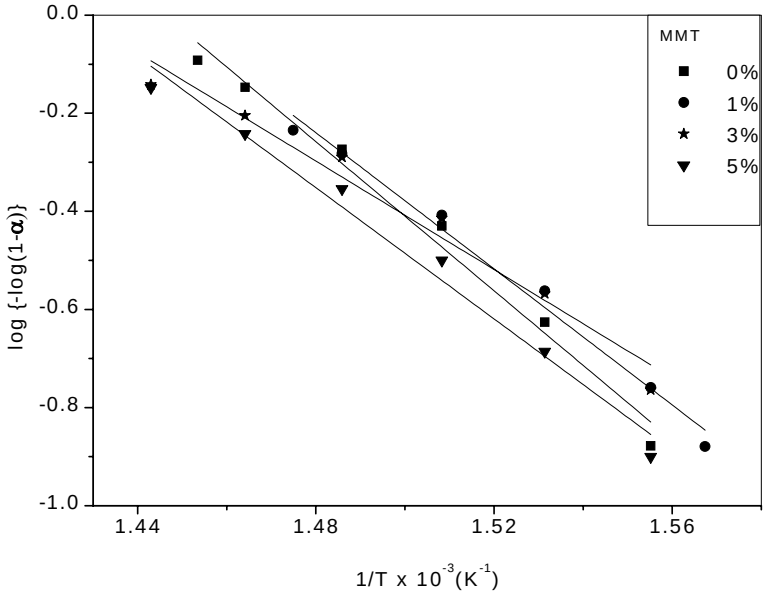

Figure-6. Plots of ln [-ln (1-α)] versus 1/T using broido´s method for epoxy/o-MMT nanocomposites.

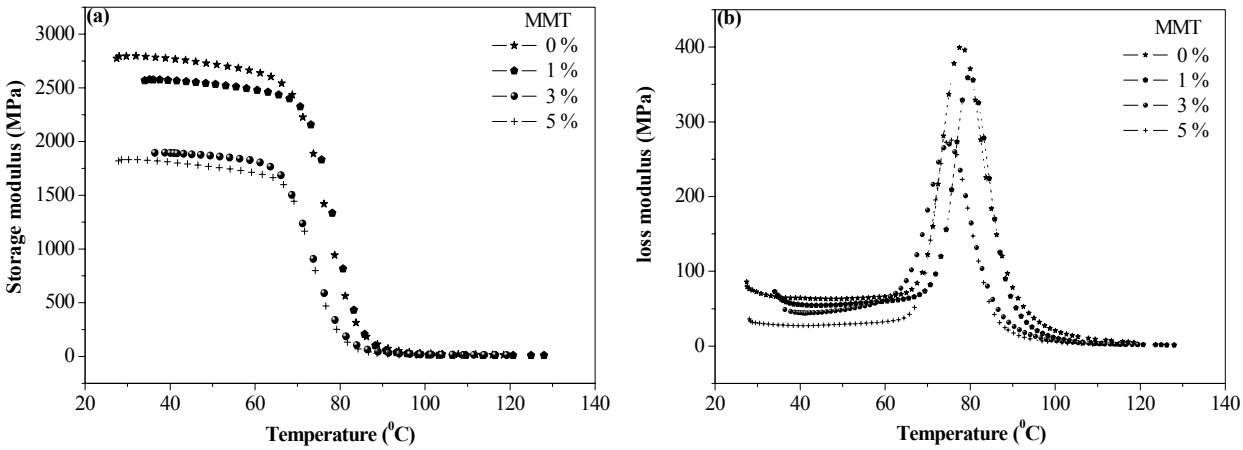

Figure-7. Plots of (a) Storage modulus and (b) loss modulus as a functional of temperature for epoxy/o-MMT nanocomposites.

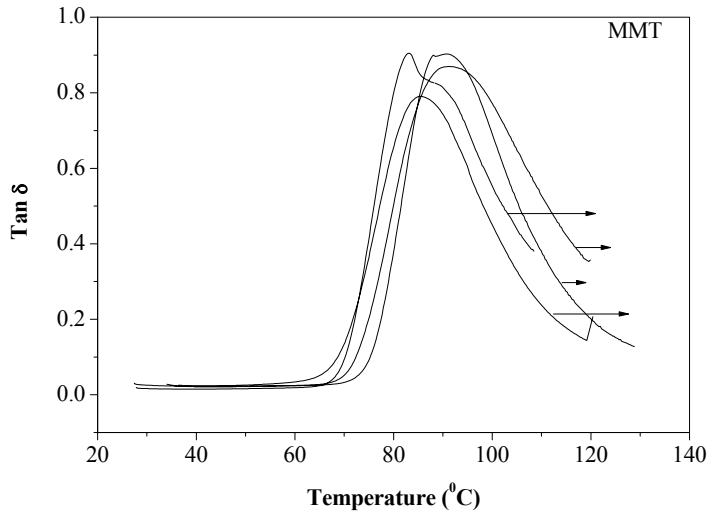

Figure-8. Complex young's moduli of epoxy /o-MMT nanocomposites.

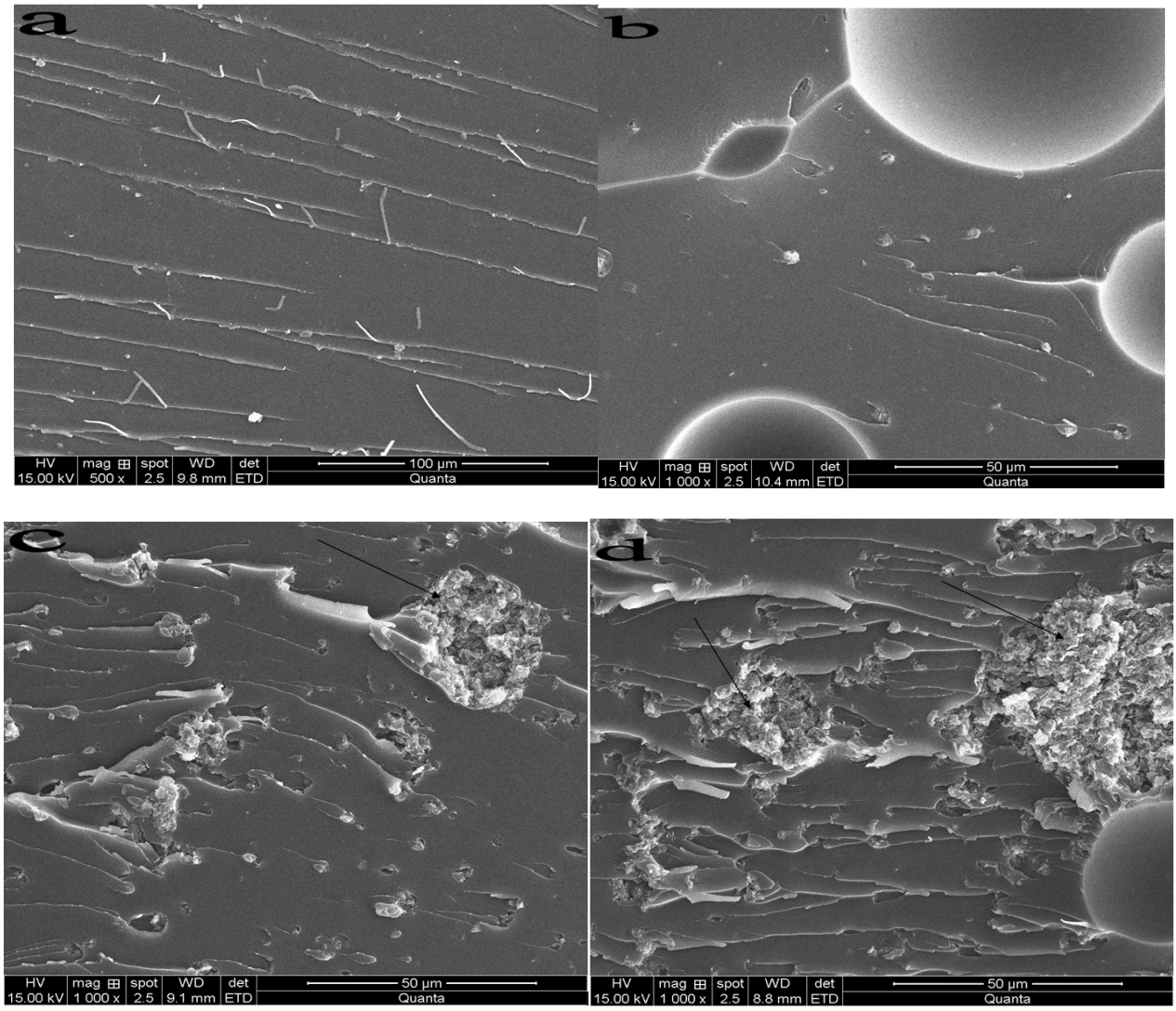

Figure-9. SEM images of (a) 0 %, (b) 1 %, (c) 3% and (d) 5% o-MMT loaded epoxy nanocomposites.

5. CONCLUSIONS

A marked improvement in tensile properties was found with increase in organo clay content in the composite. The thermal stability and degradation kinetics of epoxy /MMT nanocomposites have been reported in this research investigation. TGA thermograms indicates that all epoxy nanocomposites are stable upto 221 °C and undergo one step thermal degradation in the temperature range 221-505°C. It can be observed that the thermal stability of the nanoclay loaded epoxy composites is slightly high as compared to neat epoxy. Kinetic parameter (E_a) of thermal degradation process was evaluated by using Coats-Redfern and Broido methods. Introduction of the nanoclay (inorganic) phase into epoxy matrix increases the thermal stability, and affects the total heat of degradation, which suggests a change in the degradation reaction mechanism. Kinetic studies reveal that the activation energy calculated by both methods is comparable. Lowest activation energy values were observed for nanocomposites as compared to neat epoxy. The DMA and DSC have been shown that T_g decrease very slightly with increasing MMT. The SEM has been shown the 1 wt. % MMT particles dispersed well within the polymeric matrix. The aggregation surface of 5 wt. % was revealed.

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