

# Thermal Characteristics of Nanostructured Filler incorporated Polyvinyl Ester Nanocomposites

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**Abstract:** Vinyl ester resin nanocomposites were synthesized with organically modified layered silicates (o-montmorillonite, o-MMT) (organoclays) by in situ polymerization. The prepared vinyl ester/o-MMT composites have been characterized for mechanical properties such as tensile properties and impact strength. Thermal characteristics of the vinyl ester/o-MMT nanocomposites were evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermal degradation kinetic parameter of the nanocomposites evaluated by using three mathematical models namely, Horowitz–Metzger, Coats–Redfern and Broido's methods.

**Keywords:** polyvinyl ester, montmorillonite, composite, thermal properties, degradation kinetics.

## Introduction

Polymer-based nanocomposites consist of thermoset, thermoplastic or elastomeric matrices reinforced with nanoparticles or nanofibres. These materials are of great interest from an industrial and scientific perspective because they show much better behaviour and characteristics in comparison with conventional composites [1-2]. Vinyl ester resin is a thermosetting polymer used widely in advanced composite manufacturing processes such as hand lay-up, pultrusion and resin infusion. Vinyl ester resins give high performance composites at low cost and these composites possess superior material properties, compared to most unsaturated polyesters[3]. Glass fibre reinforced vinyl ester resins are also increasingly used for military and commercial applications due to good toughness, excellent chemical resistance and good mechanical

properties [4-5]. Nanocomposites are a class of composites in which the reinforcing phase dimensions are in the order of nanometers[6]. Layered materials are potentially well suited for the design of hybrid nanocomposites, because their lamellar elements have high in-plane strength, stiffness and a high aspect ratio [7]. The smectic clays (e.g., montmorillonite) and related layered silicates are the materials of choice for polymer nanocomposite design for two principal reasons: (i), they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale. (ii), they occur ubiquitously in nature and can be obtained in mineralogically pure form at low cost. The layered clay-polymer nanocomposites can be prepared by replacing the hydrophilic Na<sup>+</sup> and Ca<sup>+</sup> exchange

cations of the native clay with more hydrophobic onium ion to form a polymer-clay hybrid through two ways. The first is the intercalation of a monomer into the clay interlayer and subsequent heat treatment for polymerization[8]. The second is the direct intercalation of a preformed polymer into the layered clay[9]. Since the development of nylon-6-clay nanocomposite by Toyota researchers[10], extensive studies on polymer-clay nanocomposites have been investigated in order to obtain new organic-inorganic nanocomposites with enhanced properties. The use of clay or organically modified clay as precursors for preparation of nanocomposites has been studied into various types of polymer systems including polyamide 6 (PA) [11], epoxy[12], polyimide (PI)[13], polyester [14], polypropylene (PP)[15], polystyrene (PS)[16], polyethylene oxide (PEO)[17], polycaprolactone [18] and polymethyl methacrylate (PMMA)[19].

Gilman et al have investigated the nanocomposites of vinyl esters and showed formation of intercalated composites with 25-39% reductions in peak heat release rate (PHRR), and equally significant reductions in mass loss rate (MLR), and average heat release on rate (AHRR), for samples prepared by mixing for a specific time in air[20].

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[21-22]. Brown et al[21], and Feng et al [22] studied the  $T_g$  of epoxy/organoclay nanocomposites using dynamic mechanical analysis (DMA).

The objective of this research article is the influence of o-MMT concentration on mechanical and thermal behavior of vinyl ester/o-MMT nanocomposites. Thermal degradation kinetic parameters such as energy of activation ( $E_a$ ) have been calculated for the nanocomposites using three mathematical models namely; Horowitz-Metzger[23], Coats-Redfern [24] and Broido's [25] methods and the results are compared.

## Experimental

### Materials

The resin used to prepare composite was general purpose vinyl ester, VRP-2121, obtained from M/s. Vikram Polymers and Resins, Bangalore, India. The typical properties of vinyl ester are viscosity is 650 cPa at 25°C and specific gravity is 1.125 at 25°C. Methyl ethyl ketone peroxide (MEKP) was used as catalyst and cobalt octoate as promoter, and these were procured from M/s.

Swathi Chemicals, Bangalore, India. Organically modified montmorillonite (Nanomer I.31PS) was obtained from Sigma, Bangalore. It is surface modified MMT clay: (Na)-modifiers-gamma-aminopropyl triethoxysilane, octadecylamine - CEC ~145 meq/100 g, i.e., (MMT) and specific gravity is 2.53 at 25°C. All other chemicals used in this study are AR grades.

### Preparation of nanocomposite

Vinyl ester resin nanoclay composites were prepared by using in-situ polymerization method. In this investigation, nanoclay was swollen in vinyl ester resin. Different amounts viz., 0, 1, 3 and 5 wt. % of organo MMT were mixed with the vinyl ester resin by means of a mechanical stirrer for 3 h at room temperature to obtain a homogenous mixture. Upon completion of degassing, the vacuum was released, MEKP and cobalt octoate were added at a ratio of 100:1.4:1.4 by weight while stirring slowly. The liquid mixture was then cast in a preheated cleaned and 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 80 °C for 4 h. The post cured vinyl ester composite laminates were left in the oven and allowed to cool gradually to ambient temperature before removal from the moulds. The cured vinyl ester laminates were machined into different dimensions as per the standard specifications for characterization by different methods.

### Techniques

The prepared vinyl ester/o-MMT composites were characterized for physical properties such as density and surface hardness according to ASTM D 785 and ASTM D 2240 methods respectively. The tensile behavior of the blends were measured using JJ Lloyds Universal Testing Machine, model Z20, 20 KN, USA as per ASTM D-638 test method at a crosshead speed of 50 mm/min and a gauge length of 50 mm. The test specimens were rectangular in shape with dimensions 120 x 15 x 3 mm<sup>3</sup>. Minimum five samples were tested at room temperature for each formulation and the average values are reported. Charpy impact strength (unnotched) was measured in a WinPEN CEAST S. p. A., Italy according to ISO 179. The transition temperature of the samples were examined by using differential scanning calorimeter (DSC) model DSC-Q 200, DuPont TA instrument, USA. All samples were sealed in hermetic aluminum pans. The thermal behaviours of the samples were investigated at the heating rate of 10 °C/min from ambient to 300 °C under nitrogen gas flow of 60

mL/min. The thermal stability of the vinyl ester/MMT nanocomposites have been evaluated using DuPont TA Instrument, USA with TGA-Q 50 module. The instrument was calibrated using pure calcium oxalate sample before analysis. About 6-8 mg of sample was used for dynamic TGA scans at a heating rate of 20 °C/min in the temperature range of ambient to 700 °C in nitrogen gas purge. The TG curves were analyzed as percentage weight loss as a function of temperature. The oxidation index (OI) was calculated based on the weight of carbonaceous char as related by the empirical equation;

$$\text{OI} \times 100 = 17.4 \times 0.4 \text{ CR} \quad (1)$$

The thermal degradation kinetic parameters were determined for vinyl ester/MMT nanocomposites using Horowitz–Metzger (HW) (23), Coats–Redfern (CR) (24) and Broido's (BR) (25) methods which provide overall kinetic data. The Horowitz–Metzger relation used to evaluate the degradation kinetics is;

$$\ln [\ln (W_0 - W_f) / (W - W_f)] = E_a \theta / RT_s^2 \quad (2)$$

where,  $W_0$  is the initial weight of the sample,  $W_f$  is the final weight of the sample,  $W$  is the weight remaining at a given temperature,  $T$ ,  $E_a$  is the activation energy,  $\theta = T - T_s$ ,  $T_s$  is the DTG peak temperature and  $T$  is the temperature corresponding to weight loss. Plot of  $\ln[-\ln(1-\alpha)]$  versus  $\theta$  should give a straight line whose slope is  $E_a/RT_s^2$ . Coats–Redfern (CR) [25] relation is as follows;

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

where,  $\alpha$  is the fraction of sample decomposed at temperature  $T$ ,  $T$  is the derivative peak temperature,  $A$  is the frequency factor,  $\beta$  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) method is as follows;

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

where,  $(1-\alpha)$  is the fraction of number of initial molecules not yet decomposed,  $T$  is the peak temperature of the derivative curve of TG,  $R$  is the

gas constant and  $E_a$  is the activation energy can be calculated from the plot of  $\log (-\log(1-\alpha))$  versus  $1/T$ .

## Results and Discussion

The measured physico-mechanical properties such as density, surface hardness and tensile behaviors of vinyl ester/o-MMT composites are nominated in Table 1. From Table 1 it is clear that pristine vinyl ester resin cast had an average density of 1.19 g/cc. After incorporating nanoclay, an increase in the density of the composites was observed. This increase in density of the composites is attributed to the incorporation of high density nanofiller (2.53 g/cc) in low dense vinyl ester matrix. The density values of the nanocomposites increases with increase in filler content and it lies in the range 1.199 – 1.23 g/cc. The theoretical density was calculated for nanocomposites by weight additive principle, which states that:

$$d = w_1d_1 + w_2d_2 \quad (5)$$

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 slightly higher compared to corresponding experimentally obtained values (Table 1). The actual density ( $d_{ce}$ ) of the composite can be determined experimentally by simple water immersion technique. The volume fraction of voids ( $V_v$ ) in the composites is calculated using the following equation:

$$V_v = \frac{(d_{ct} - d_{ce})}{d_{ct}} \quad (6)$$

The theoretical and measured densities of the composites along with the corresponding volume fraction of voids are presented in Table 1. It may be noted that the composite density values calculated theoretically from weight fractions using Eq.(5) are not equal to the experimentally measured values. This difference is a measure of voids and pores present in the composites. It is clearly seen that with the addition of MMT as the filler material, more voids are found in the composites. The calculated void content of the composites lies in the range 0.3-2.1 %. As the filler content increases from 0 wt% to 5 wt% the volume fraction of voids is found to be increasing. Density of a composite depends on the relative proportion of matrix and reinforcing materials and this is one of the most important factors determining the properties of the composites. The void content is the cause for the difference between the values of true density and the theoretically calculated one. The voids significantly affect some of the mechanical properties and even the performance of composites in the workplace. Higher

void contents usually mean lower fatigue resistance, greater susceptibility to water penetration and weathering resistance[26]. The knowledge of void content is desirable for estimation of the quality of the composites. It is understandable that a good composite should have fewer voids.

This may be due to void formation and poor interfacial adhesion between matrix and nanofiller in the nanocomposites.

Surface hardness is a property measured laterally, whereas the modulus is measured longitudinally. The measured values of shore D hardness are given in Table 1. From the table it can be seen that, the surface hardness values of vinyl ester and its composites shows 65 to 73 shore D respectively. From the table it can be observed that, the incorporation of MMT into vinyl ester shows significant improvement in surface hardness of composites. 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[27].

Mechanical properties of nanocomposites generally depend on factors such as filler content, particle size and shape, the degree of adhesion between the filler and the polymer matrix and the dispersion degree of the filler within the matrix. From Table 1 it was noticed that much lower values of tensile strength and tensile elongation were obtained than those of pristine vinyl ester. Tensile strength and percentage of elongation at break of vinyl ester/o-MMT markedly reduced from 8.3 MPa to 3.2 MPa and from 1.93 to 0.62 respectively with increase in o-MMT content, which is not surprising, considering micro-scale dispersion of clay particles and no polymer – filler tethering. The tensile modulus markedly increases from 2736 to 3258 MPa on increasing the organically modified o-

MMT content from 0 to 5 wt % in vinyl ester matrix.

The impact strength evaluation is an important parameter to study the toughening behavior of polymer nanocomposites. The influence of nanoclay incorporation into vinyl ester on the impact strength of vinyl ester/o-MMT nanocomposites is shown in Figure 1. The impact strength of the nanocomposites is higher than pristine vinyl ester (12 kJ/m<sup>3</sup>). From the figure it was noticed that a noticeable improvement in impact strength of the composites as increase in filler content upto 3 wt.% and further increase in filler content slightly reduces the impact strength.

Differential scanning calorimetry (DSC) measured the glass transition of the vinyl ester/o-MMT nanocomposites. The DSC thermograms of pristine polyvinyl ester and vinyl ester/o-MMT composites are shown in Figure 2. The  $T_g$  is taken at the median point in the range of glass transition, and the results are presented in Table 2. From the figure it can be observed that the  $T_g$  values of nanocomposites were lies in the range 93-103 °C. The  $T_g$  of nanocomposites are slightly lower than unfilled vinyl ester. 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[28-29]. Xu et al[28] measured  $T_g$  of epoxy/o-MMT nanocomposites using DMA 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 [29].

**Table 1: Physico-mechanical properties of vinyl ester/o-MMT nanocomposites**

MMT content in vinyl ester (wt %)	Density (g/cc)		Void Content (%)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
	Expt.	Theor.				
0	1.190	-	-	2736	8.3	1.93
1	1.199	1.203	0.3	3031	5.3	1.03
3	1.209	1.23	1.7	3204	3.3	0.63
5	1.230	1.257	2.1	3258	3.2	0.62

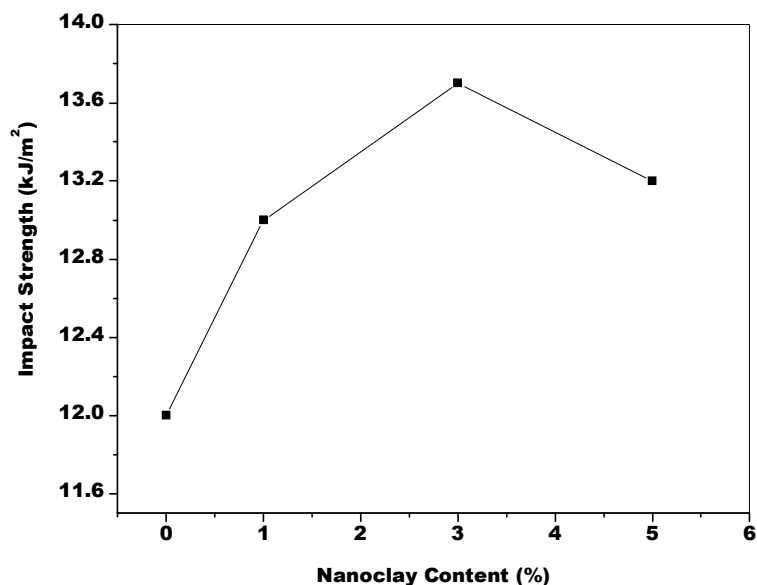


Fig. 1: Influence of nanoclay content on impact strength of vinyl ester/o-MMT nanocomposites

Table 2: Glass transition temperature obtained from DSC

Composition of nanoclay in vinyl ester (wt. /wt. %)	T <sub>g</sub> (°C)	
	Expt	Theor
0	103.1	-
1	94.0	94.9
3	93.4	96.2
5	93.0	97.8

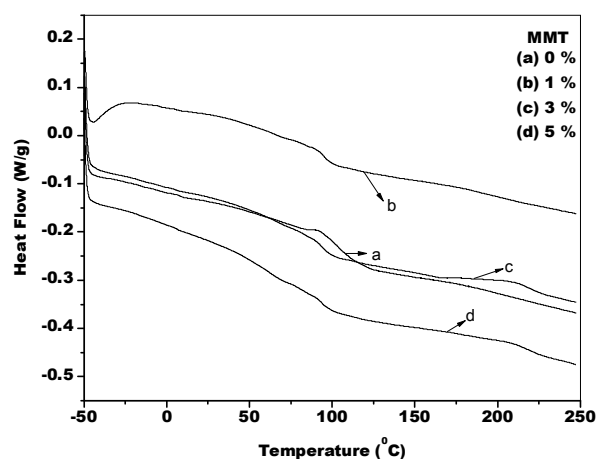


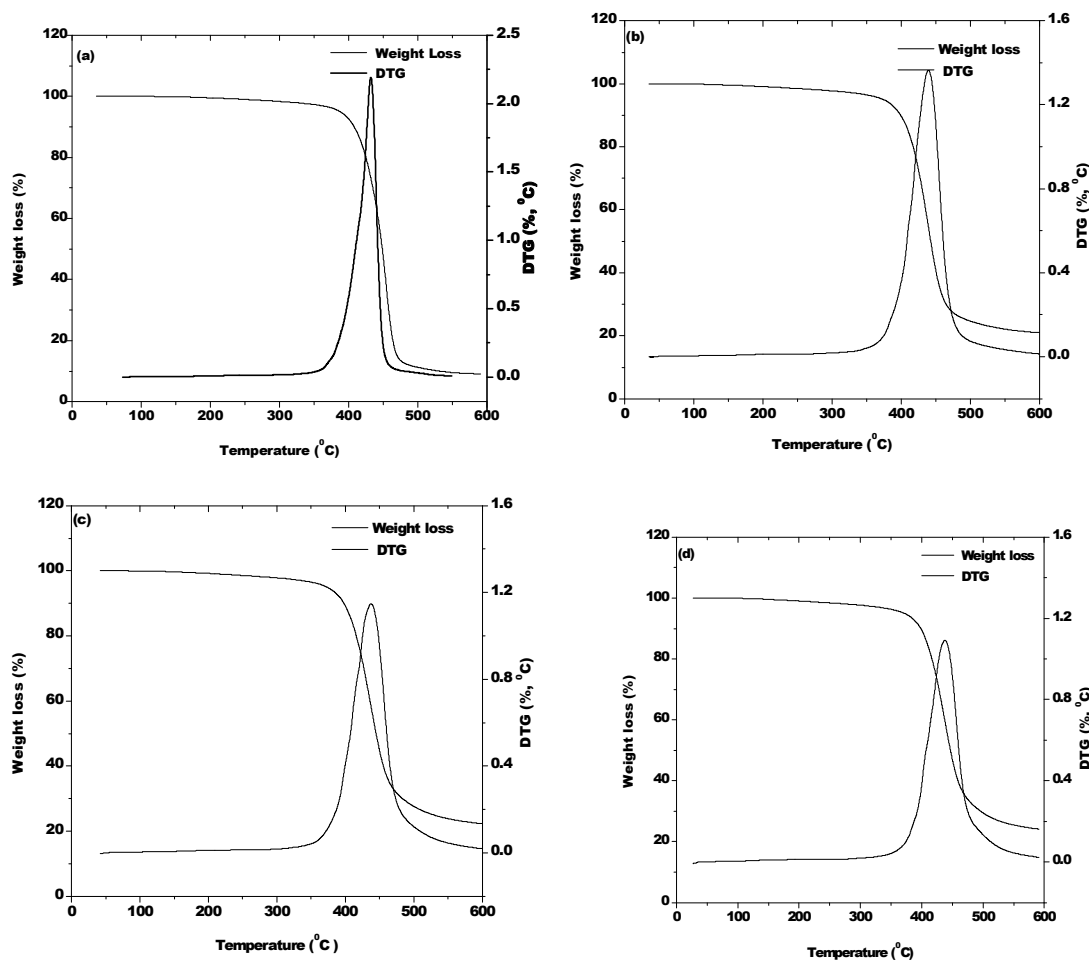
Fig. 2: DSC thermograms of vinyl ester and its nanocomposites

The TGA thermograms of 0, 1, 3 and 5 % nanoclay loaded polyvinyl ester composites are shown in Figures 3 (a)-(d) respectively along with derivative thermograms. The thermal degradation characteristics were analyzed from TGA thermograms and the data is given in Table 3. TGA thermograms of pristine polyvinyl ester indicates one step thermal degradation processes. The thermal degradation of vinyl ester resin occurred in the temperature range 290-495 °C with the major

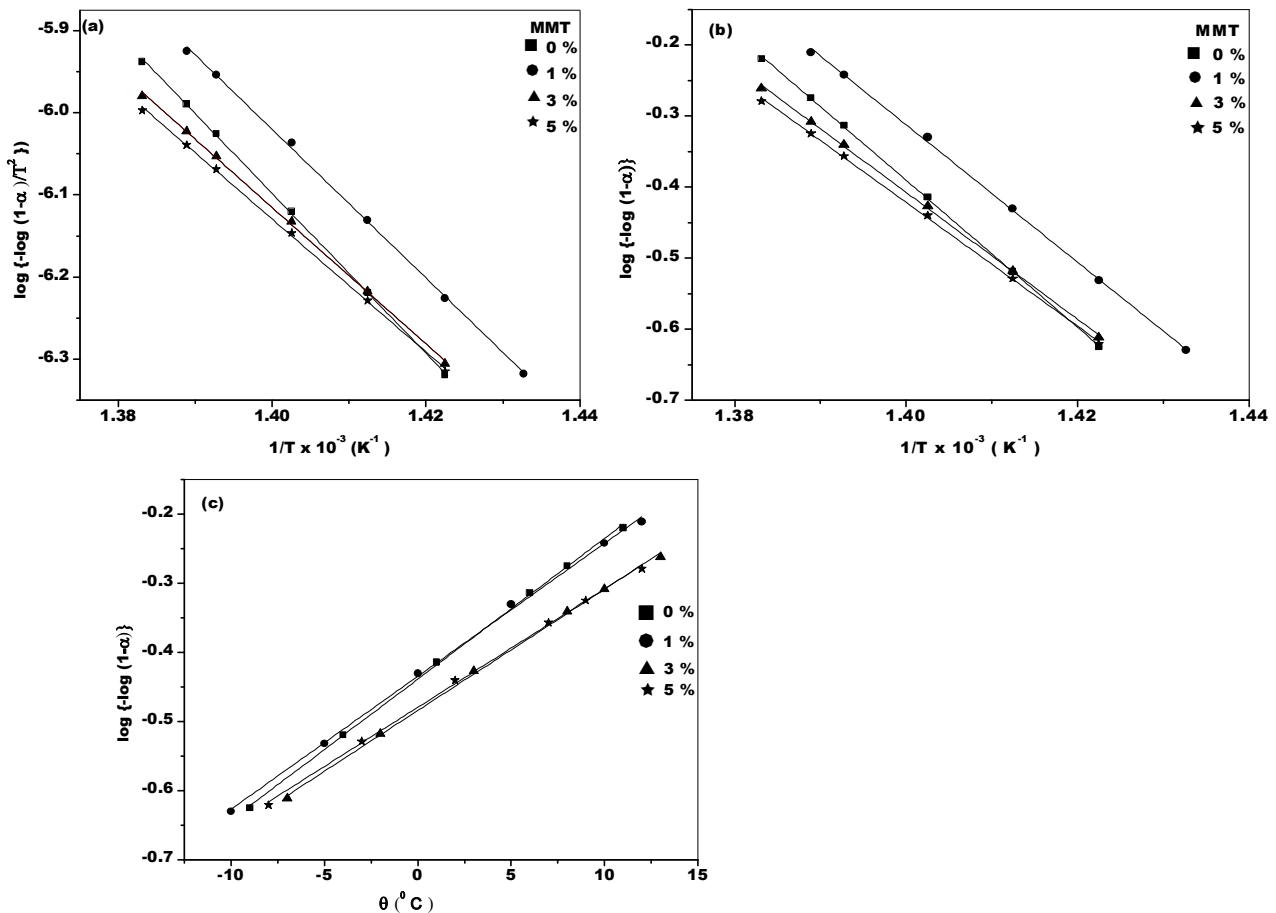
weight loss of 90.9 %. The TGA curves for all nanocomposites indicate that there is a single step thermal degradation. The decomposition temperature in this stage was started at 292 °C and takes place up to 550 °C. It was found that the pure polyvinyl ester degrades slightly faster than the nanocomposites. The onset of degradation of vinyl ester/o-MMT nanocomposites is higher than that of neat polyvinyl ester (Table 3).

**Table 3: Temperature range obtained from derivative TGA curves of vinyl ester/o-MMT nanocomposites**

MMT content in vinyl ester (wt. %)	Temperature ( $^{\circ}\text{C} \pm 2$ )			Ash content (%)
	$T_0$	$T_p$	$T_c$	
0	290	439	495	9.0
1	292	435	550	18.1
3	302	437	530	20.0
5	310	438	535	24.1

**Fig. 3: TGA and derivative thermograms of, (a) 0 %, (b) 1 %, (c) 3 % and (d) 5% MMT filled vinyl ester nanocomposites****Table 4: Thermal data obtained from TGA thermograms of vinyl ester/o-MMT nanocomposites**

Clay content in vinyl ester (wt. %)	Temperature at different weight loss ( $\pm 2^{\circ}\text{C}$ )					IDPT	Oxidation Index (OI)
	$T_0$	$T_{10}$	$T_{20}$	$T_{50}$	$T_{\max}$		
0	175	395	415	445	549	469	0.64
1	180	396	414	424	550	470	1.27
3	195	395	414	444	555	472	1.40
5	190	395	415	446	564	475	1.68



**Fig. 4:** Plots of  $\log\{-\log(1-\alpha)/T^2\}$  versus  $1/T$  using Coats-Redfern method (a), Plots of  $\log\{-\log(1-\alpha)\}$  versus  $1/T$  using Broido's method (b) and plot of Horowitz-Metzger (c) for the determination of activation energies vinyl ester /o-MMT nanocomposites

This can be attributed to the presence of o-MMT, which has relatively higher thermal stability than polyvinyl ester. The ash content in composites increases with increase in o-MMT content in the composites as expected. Ash content of o-MMT filled vinyl ester composites lies in the range 9.0-24.1 %, which is higher than the o-MMT filler loaded theoretically. This is due to TGA thermograms were analyzed under  $N_2$  gas purge and also pristine vinyl ester yields about 9 % ash content. The thermograms obtained during TGA scans were analyzed to give the percentage weight loss as a function of temperature. From TGA curves it can be clearly observed that the weight loss markedly decreases with increase in o-MMT 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

nanocomposites. The relative thermal stability of vinyl ester nanocomposites have been evaluated by comparing the decomposition temperatures at different percentage weight loss (**Table 4**). Higher the values of  $T_{10}$ ,  $T_{20}$ ,  $T_{50}$  and  $T_{max}$  higher will be the thermal stability of the nanocomposites [30]. From the table it was observed that, these values increases with increase in o-MMT content. This can be attributed to the synergistic effect of o-MMT and matrix present in the composite. Higher the values of oxidation index (OI), higher will be the thermal stability[30-31]. From the table it was observed that the oxidation index values increases with increase in o-MMT content and it lies in the range 0.64-1.68. This data indicates that the o-MMT filled polyvinyl ester composites are more thermally stable than that of pristine polyvinyl ester. Annakutty *et al* reported that, the aforesaid investigation, it can be concluded that the flame resistance of vinyl ester/o-MMT nanocomposites was slightly enhanced as the filler content increases. char yield is directly correlated to the potency of flame retardation [32]. From the aforesaid investigation, it can be concluded that the

flame resistance of vinyl ester/o-MMT nanocomposites was slightly enhanced as the filler content increases.

#### Kinetic analysis of thermal degradation

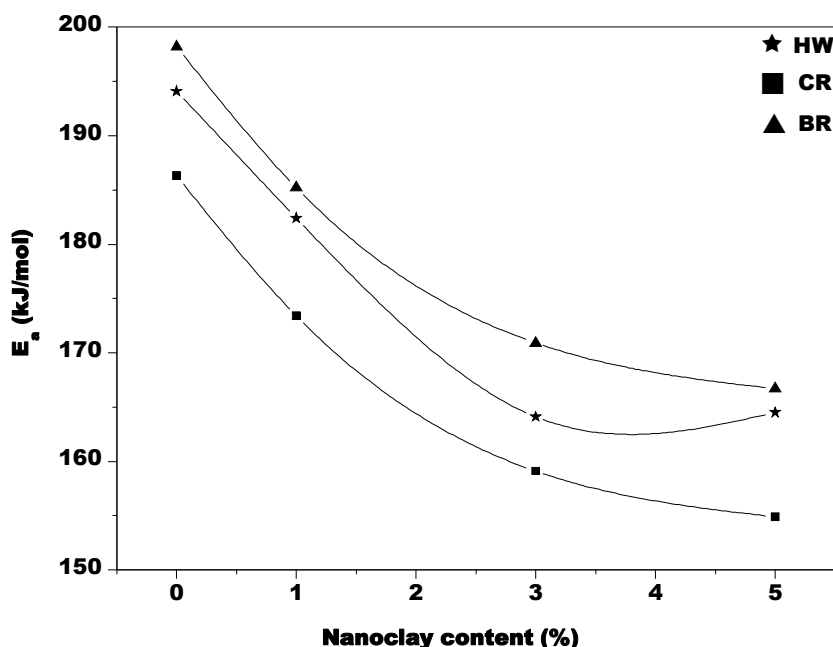
Kinetic parameters for thermal degradation properties of vinyl ester nanocomposites were evaluated from the TGA curves using Horowitz–Metzger, Coats–Redfern and Broido’s methods. The plots of  $\ln[-\ln(1-\alpha)]$  versus  $\theta$  (HM),  $\ln[-\ln(1-\alpha)]/T^2$  versus  $1/T$  (CR) and  $\ln[-\ln(1-\alpha)]$  versus  $1/T$  (BR) for vinyl ester/o-MMT nanocomposites are shown in Figures 4 (a)-(c) respectively. The regression analysis gives the slopes, constants and  $R^2$  for thermal degradation process. The linear plot with concurrency value ( $R^2$ ) closer to one was chosen for all methods. The  $R^2$  values and calculated activation

energy ( $E_a$ ) for each thermal degradation process of the composites are tabulated in Table 5.

The  $E_a$  values lies in the range 154.9-186.3 kJ/mol, 166.7 – 190.2 kJ/mol and 164.1- 189.2 kJ/mol for Coats-Redfern, Broido’s and Horowitz–Metzger methods respectively. To understand the mechanism of thermal degradation, the variation in activation energy as a function of weight percent of o-MMT content in vinyl ester is shown in Figure 5. From the figure it can be noticed that, lower  $E_a$  values for nanofiller loaded vinyl ester composites. This is due to often incorporation of o-MMT, formation of low molecular weight vinyl ester between interlayers of nanoclay, for which less energy is sufficient for degradation.

**Table 5: Activation energies calculated by Horowitz-Metzger (HM), Coats-Redfern (CR) and Broido’s (BR) methods with the respective concurrency value (R<sup>2</sup>) for vinyl ester/o-MMT nanocomposites**

MMT content(wt.%)	Activation energy ( $E_a$ ) (kJ/mol) $\pm$ 4 %					
	HW	R <sup>2</sup>	CR	R <sup>2</sup>	BR	R <sup>2</sup>
0	189.2	0.998	186.3	0.999	190.2	0.999
1	182.4	0.999	173.4	0.998	185.2	0.996
3	164.1	0.997	159.1	0.988	170.9	0.998
5	164.5	0.999	154.9	0.997	166.7	0.999



**Fig. 5: Activation energy as a function of weight percent of o-MMT in vinyl ester obtained by different methods for thermal degradation process**



## Conclusions

Vinyl ester/o-MMT nanocomposites have been prepared by in-situ polymerization method. The contents of nanoclay showed a great influence on the mechanical strength and thermal stabilities. The tensile strength of composites continually decreased with increasing of nanoclay content due to no polymer-filler tethering. However, improvement in tensile modulus and surface hardness with increase in nanofiller content in vinyl ester matrix was noticed. TGA thermograms indicates that all vinyl ester nanocomposites are stable upto 290 °C and undergo one step thermal degradation in the temperature range 290-535°C. Kinetic parameters of thermal degradation were evaluated by using Horowitz–Metzger, Coats-Redfern and Broido methods. Introduction of the

nanoclay (inorganic) phase into vinyl ester 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 three methods is comparable. Lowest activation energy values were observed for nanocomposites as compared to neat polymer. The DSC and TGA data exhibited that the dispersed nanolayers of the clays in the vinyl ester polymer matrix led to a slight decrease of  $T_g$ , but the thermal stabilities of the nanocomposites were significantly improved with the presence of the clays. The results indicate that o-MMT concentration affects the state of dispersion, which has a dominating influence on the thermal and mechanical properties.

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