

**ChemTech**International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol. 3, No.3, pp 1292-1301, July-Sept 2011

Investigation on Thermal and Mechanical Behaviours of Crysnanoclay Incorporated Polyamide/ Nanoclay Composites

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Abstract: Polyamide is extensively used in engineering application because of its unique characteristics such as low price, low viscosity, high toughness, shelf lubricating behaviour better sunlight resistance, abrasion resistance and high chemical resistance. This study focuses on achieving high stiffness/strength characteristic of nylon 66/NC nanocomposites, prepared via melt compounding by twin screw extruder. Mechanical test results indicated that all composites exhibited higher stiffness than pristine nylon 66. Thermal characteristics were performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). TGA thermograms indicate a significant increase in thermal stability after incorporation of crysnanoclay additives to nylon 66 matrixes. A slight increase in HDT and marked increase in izod impact strength after incorporation of crysnanoclay into nylon 66 composite was observed. The activation energy of degradation was determined using three mathematical models namely; Horowitz–Metzger, Coats–Redfern and Broido's methods and the results are compared.

Keywords: Polyamide 66, nanocomposites, mechanical performance, thermal characterization, crysnanoclay.

Introduction

Polymer/layered silicates nanocomposites have received a great deal of attention since their first demonstration by the Toyota group in 1987 [1]. These nanocomposites exhibit superior properties such as higher tensile strength, modulus, heat resistance, light weight, and less permeability to gas at a lower level

of loading relative to conventionally scaled composites. Nowadays, the preparation system of layered silicate nanocomposites is very abundant, many surfactants are used to modify montmorillonite [2-4], such as amino- dodecanoic acid, octadecylammonium etc., while no work has been reported to guide the selection of surfactants for different polymers and different processing methods

systematically. Nylon 66 is a versatile engineering plastic; the successful development of nylon 6 nanocomposites inspired us to study nylon 66/montmorillonite nanocomposites. There are few reports involving nylon 66 nanocomposites some of which show that relative to nylon 6, nylon 66/montmorillonite hybrids show fewer enhancements [5]. The mechanical property improvements were ascribed to the enhanced polymer – clay interaction. Other than in – situ polymerization, a more economical and simple conventional polymer melt compounding process can also accomplish the incorporation of clay into thermoplastic matrices. Nevertheless, there are only a few studies on formation of polyamide/clay nanocomposites by direct melt compounding and most of them are concentrated on nylon 6/clay nanocomposites [6]. The derivation of kinetic data in the study of PU decomposition using TGA has received increasing attention in the last decade [7]. Kinetic data obtained from TGA is very useful for understanding the thermal degradation processes and mechanisms, used as input kinetic parameters through the course of the degradation and of the relationship of the data obtained in the process to other interesting properties. Kinetic studies also help to identify whether or not a stabilizer, filler or an additive helps to improve the thermal stability of a material. The values for activation energy and reaction order obtained depend on atmosphere, sample mass, sample shape, flow rate, heating rate, and the mathematical treatment used to evaluate the data [8]. Research on nylon 66/clay nanocomposites was mainly focused on the crystallization and phase transition behaviour of nylon 66 with inclusions [9,10]. In this paper, we explore nylon 66 nanocomposites prepared by melt compounding and also investigate the thermal stability and mechanical properties of nanocomposites with varying clay content. Degradation kinetic parameters such as energy of activation (E_a) were calculated for the nanocomposites using three mathematical models namely; Horowitz–Metzger [11], Coats–Redfern [12] and Broido's [13] methods and the results are compared.

Experimental

Materials

Polyamide 66 (PA66) pellets (Brand name: EPR32, with relative viscosity of 3.2) was obtained from GSRC India. The Crysmano 1030 is a natural montmorillonite mineral modified with quaternary ammonium salt. The typical properties of Crysmano 1030 are d-value – 19 nm at 25°C and specific gravity

- 1.97 at 25°C. Compositions and designations of the studied materials are listed in **Table 1**.

Preparation of nanocomposites

Nylon 66 pellets and crysnano clay were oven-dried at 85 °C for 24 h. Then the desired proportions (see below) of the ingredients were mixed and melt compounded in a Bearstoff ZE40A twin-screw extruder 40 mm screw. Extrusion was performed within the temperature range 260 – 280 °C and a screw speed of 300 rpm. Subsequently, the extruded pellets were oven-dried and moulded into dog-bone and rectangular bars by using a DEP Windor 75 T. The barrel and mould temperatures of the injection moulding machine were maintained at 280°C. A series of preparation of NC and PA66 was carried out by Drum tumliyi. Melt blending in a Brabender at a speed of 40 rpm at 280°C for 5 min. In the case of preparing PA66 with clay, the addition of the materials to the Brabender was in the following sequence: Adding clay to the PA66 melt mixing for two minutes at 280°C.

Characterization

The prepared polyamide/ NC nanocomposites were characterized for physical properties such as density and surface hardness according to ASTM D 785 and ASTM D 2240 methods respectively. The tensile behaviour of the composites were measured using JJ Lloyds Universal Testing Machine, model Z20, 20 KN, USA as per ASTM D-638 method at a crosshead speed of 50 mm/min and a gauge length of 50 mm. Minimum five samples were tested at room temperature for each formulation and an average values are reported. Charpy impact strength (unnotched) was measured in a WinPEN CEAST S. p. A., Italy according to ISO 179. The heat distortion temperature (HDT) of the specimens was examined according to ASTM D48-95 by a heat distortion temperature machine (CS-107, Costom Scientific Instruments, and USA). The thermal stability of the polyamide /NC nanocomposites has 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 oxidation index (OI) was calculated based on the weight of carbonaceous char as related by the empirical equation;

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

The thermal degradation kinetic parameters were determined for nylon 66 and nylon 66/NC nanocomposites using Horowitz–Metzger [11], Coats–Redfern [12] and Broido's [13] methods which

provide overall kinetic data. For the sake of calculations and to know the nature of the decomposition, the complete thermogram was divided into distinct sections according to their degradation processes.

The kinetic and thermodynamic parameters of thermal degradation process have been calculated using three models. The Horowitz–Metzger (HM) [11] relation used to evaluate the degradation kinetics is;

$$\ln [\ln (W_0 - W_t^f) / (W - W_t^f)] = E_a \theta / RT_s^2 \text{ -----(2)}$$

where, W_0 is the initial weight of the sample, W_t^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 θ should give a straight line whose slope is E_a/RT_s^2 . Coats–Redfern (CR) [12] relation is as follows;

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

where, α is the fraction of sample decomposed at temperature 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) [13] method is as follows;

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

where, $(1-\alpha)$ 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), DuPont TA instrument, USA, with model 2980-DMA. DMA thermograms were recorded in tension mode at 5 Hz frequency at a heating rate of 3°C/min in the temperature range 30 - 160 °C.

Results and Discussion

Physico - mechanical properties of the nanocomposites

The measured physico-mechanical properties such as density, surface hardness and tensile

behaviours of nylon 66/ CN nanocomposites are nominated in Table 2. From Table 2 it is clear that pristine nylon 66 cast had an average density of 1.122 g/cc. After incorporating nanocrystal, an increase in the density of the composites was observed. This increase in density of the composites is attributed to the incorporation of high dense nanofiller (1.97 g/cc), in low dense polyamide matrix. The density value of the composites lies in the range 1.122 – 1.138 g/cc. 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.

Surface hardness is a measure of resistance to indentation. Surface hardness indicates the degree of compatibility and crosslink density. A slight increase in surface hardness from 63 to 67 shore D after incorporation of nanocrystal into nylon 66 matrix was noticed. The nanocrystal effectively restricts the indentation and increases the hardness of the composites [14].

The impact strength of pristine nylon 66 is 49 J/m and improved in impact strength was noticed after incorporation of crysnanoclay. A drastic improvement obtained in impact strength after corporation of crysnanoclay into nylon 66. It is increased 6% after incorporating 5 wt% into matrix polymer.

The tensile behaviour is almost in agreement with earlier reinforced thermoplastic studies [15]. The effects of clay on the mechanical properties are shown in Table 2. The value of the modulus of the composites increases with the weight percentage of clay indicating a good dispersion of clay in the polymer. The Young's modulus of the composites increases with clay content. It is noteworthy that tensile modulus increased by 29% and tensile strength 11% with the addition of 5wt% clay to PA66 [16]. The role of clay as a reinforcing agent in PA66 matrix is clearly manifested. The elongation at break of the nanocomposites decreases from about 62% for 5 wt% NC, indicating that the plastic deformation of matrix is severely curtailed with incorporation of clay leading to embrittlement.

Table 2 shows that the heat distortion temperature of nanocomposites increases after incorporating crysnanoclay into matrix polymer. Heat distortion temperatures of PA 66, PA 66/3% CN and PA 66/5% CN are 200 °C, 235 °C and 245 °C, respectively. The heat distortion temperature of nanocomposites is much higher than that of neat PA 66. The crysnanoclay is highly crystalline material that can even improve the heat distortion temperature of the polymer matrix.

Table 1: Composition of the studied materials in wt%.

Material designation	Crysnanoclay
PA66	0
PA 66/3%NC	3
PA 66/5%NC	5

Table 2: Mechanical properties of nylon 66/ NC nanocomposites

NC content in PA 66 (wt %)	Density (g/cc)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Izod impact notched	HDT 0.45 (MPa)	Surface hardener Shore D (\pm)
0	1.122	2734	78	9.15	49	200	63
3	1.136	3576	85	2.90	51	235	66
5	1.138	3869	88	3.39	68	245	67

Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) is a useful technique to determine the quantitative degradation based on the weight loss of a composite material as a function of temperature. The typical TGA and their derivative thermograms for CN filled nylon 66 composites are shown in Figures 1 (a-c). The nylon 66 and nylon 66/CN nanocomposites were stable up to 359°C. The TG curves of PA 66 and its composites at a heating rate of 10 °C/min in N₂ atmosphere, shown in Figures 1, also exhibit single-stage degradation with well defined initial and final degradation temperatures. With the addition of only 5 %, the thermal degradation temperature value shift to higher temperature. A shift of 4 °C can be observed in the case of the clay filled into matrix polymer. The decomposition of pristine PA66 (Figure 1a and Table 3) occurs in the range of 359- 504 °C with one DTG peak at 463 °C. The thermal degradation of nylon 66/NC occurred in the temperature range 260-508°C and 364 – 509 °C, respectively. Ash content of nanocrystal filled polyamide composites lies in the range 1.04-2.98 % (Table 3).

TGA data relating to the temperatures corresponding to initial weight loss, such as T₀ (temperature of onset decomposition), T₁₀ (temperature for 10% weight loss), T₂₀ (temperature for 20% weight loss), T₅₀ (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 PA 66 nanocomposites have been evaluated by comparing the decomposition temperatures at different percentage weight loss (Table 4). Higher the values of T₁₀, T₂₀, T₅₀ and T_{max} higher will be the thermal stability of the composites [17]. From the table it was observed that, the PA 66/CN value is more than all compositions (Table 4). From Table 4, it can be observed that, PA 66 composites showed which onset degradation values of nylon 66/5% CN are higher than of pristine PA 66 and PA 66/3% CN. Higher the values of oxidation index (OI), higher will be the thermal stability [17, 18].

From the Table 4 it was observed that the oxidation index values of composites are higher than pristine PA 66 and it lies in the range 0.02 -0.19. This data indicates that the crysnanoclay filled nylon 66 composites are more thermally stable than that of pristine PA 66. PA 66 composites under investigation do not break down in a simpler manner; there may be change in chemical composition and morphological structure of Pus at each and every degradation step of pyrolysis that affects the rate of decomposition. The presence of the crysnanoclay enhanced the onset of thermal degradation because of polymer-filler interaction, exfoliation, uniform dispersion and high thermal stability of the layered silicates [19].

Table 3: Thermal degradation temperature range obtained from derivative TGA curves of nylon 66/NC nanocomposites

NC content in PA 66 (wt %)	Degradation stage	Temperature range (°C) ±2			Weight loss (%)
		T ₀	T _p	T _c	
PA 66	I	359	463	504	98.96
	Ash	-	-	-	1.04
PA 66/ NC 3%	I	360	464	508	97.6
	Ash	-	-	-	2.4
PA 66/ NC 5%	I	363	465	509	97.02
	Ash	-	-	-	2.98

Table 4: Thermal data obtained from TGA thermograms of nylon 66/NC nanocomposites

NC content in nylon 66 (wt %)	Temperature at different weight loss (± 4 °C)					IDPT (°C) ±2	Oxidation Index (OI)
	T ₀	T ₁₀	T ₂₀	T ₅₀	T _{max}		
PA66	387	405	437	461	492	411	0.02
PA 66/ NC 3%	390	406	438	461	514	421	0.08
PA 66/NC 5%	392	410	441	462	515	423	0.19

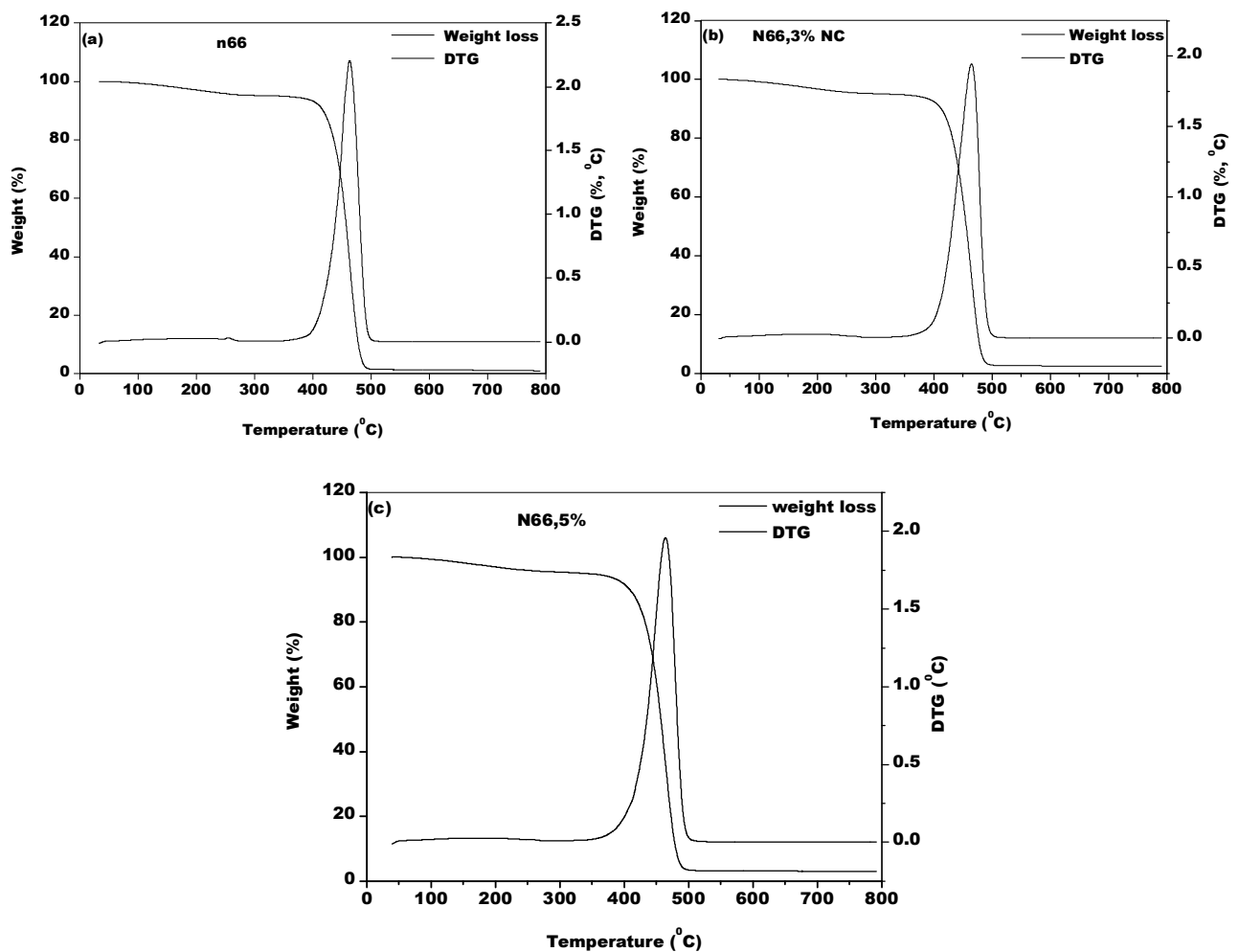


Fig. 1: TGA and derivative thermograms of, (a) 0 %, (b) 3 %, and (c) 5 % CN filled PA 66/CN nanocomposites

Kinetic analysis of thermal degradation process

Kinetic parameters were evaluated from the TGA curves using the plots of Broido (BR), Coats–Redfern (CR) and Horowitz - Metzger (HM) methods. The BR, CR and HR plots for thermal degradation process of crysnanoclay filled nylon 66 composites are shown in Figure 2. Regression analysis carried out for all the plots. The mechanism of R^2 close to unity was chosen. The regression analysis gives the results of slopes, constant and R^2 values corresponding to thermal degradation for the selected temperature range. The R^2 and calculated activation energy (E_a) values for each thermal degradation process and for each method are given in Table 5. BR, HW and CR methods have

shown comparable values of E_a . To understand the mechanism of thermal degradation, the variations in activation energy as a function of weight percent of CN content in composites are shown in Figure 3. From the figure it can be noticed that, there is no systematic variation in activation energy with composition. The lowest E_a values were observed for the nanocomposites as compared to neat polymer for all the methods. This is due to lower energy required to remove volatile components and low molecular weight materials present in nylon 66 composites. Higher E_a values were observed for nylon 66, because higher energies are required for bond scission and unzipping of nylon 66 chains.

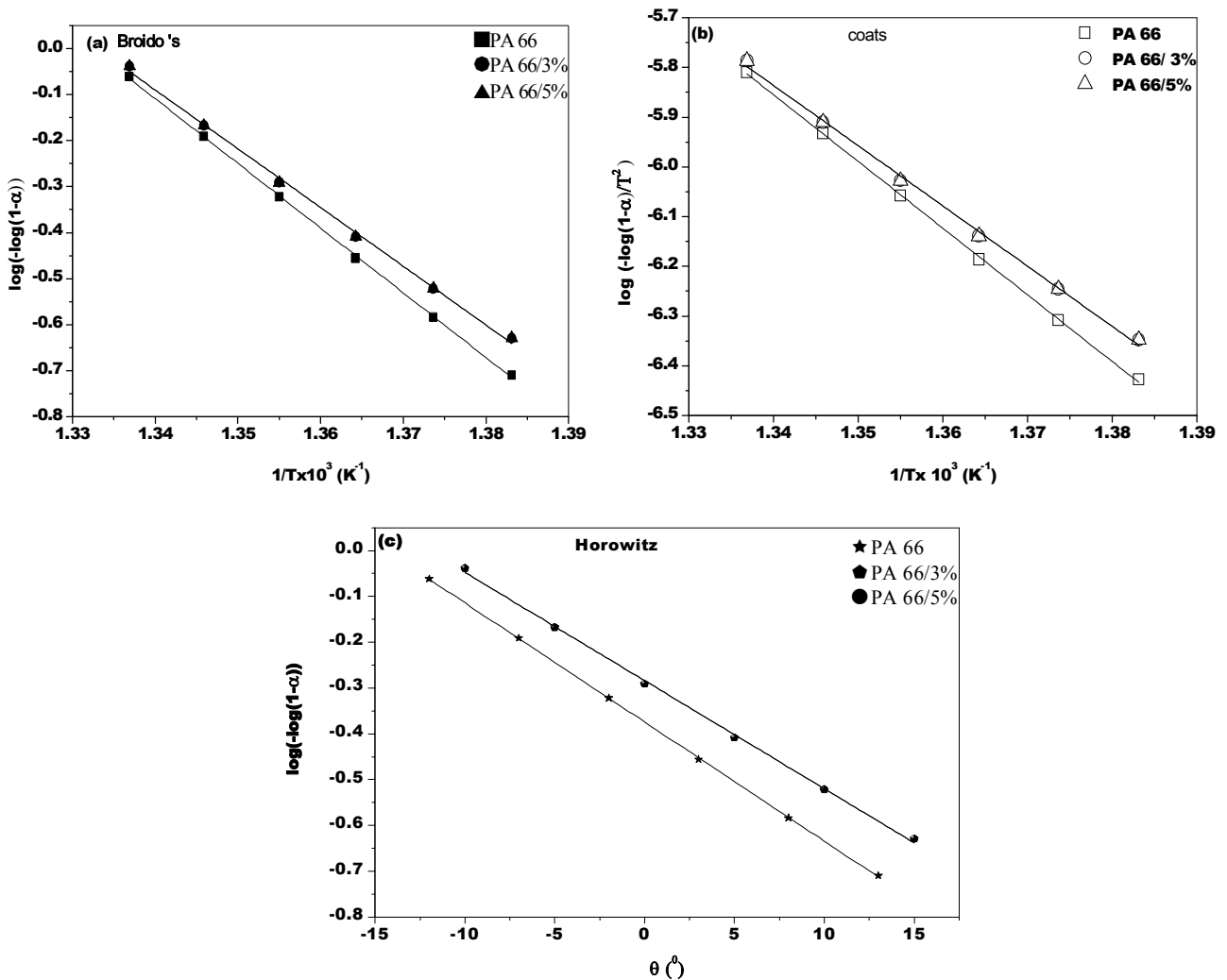
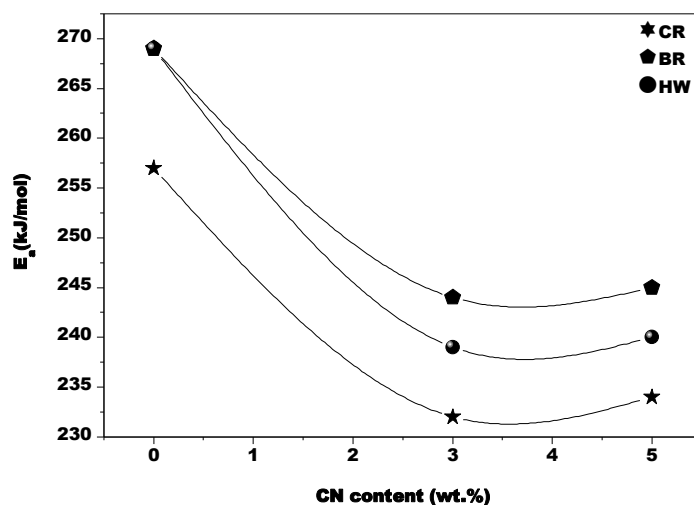


Fig. 2: (a) Plots of $\log\{-\log(1-\alpha)\}$ versus $1/T$ using Broido's method, (b) Plots of $\log\{-\log(1-\alpha)/T^2\}$ versus $1/T$ using Coats-Redfern method, and (c) plots of $\log\{-\log(1-\alpha)\}$ versus θ using Horowitz-Metzger for the determination of activation energies of PA 66/CN nanocomposites

Table 5: Activation energies calculated by Coats-Redfern (CR), Broido's (BR) and Horowitz – Metzger methods with the respective concurrency value (R^2) for nylon 66/NC nanocomposites

NC content in PA 66 (wt. %)	Activation energy (E_a) (kJ/mol) \pm 4 %					
	CR	R^2	BR	R^2	HW	R^2
0	257	0.999	269	0.999	269	0.999
3	232	0.998	244	0.998	239	0.998
5	234	0.998	245	0.998	240	0.998

**Fig. 3: Activation energy as a function of weight percent of CN in PA 66/CN obtained by different methods thermal degradation**

Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements are believed to be a good method for gaining insight into the effects exerted by the filler on the polymer matrix. These effects are displayed as a variation in dynamic storage modulus, a modification of the peak position and width of the relaxation spectrum as a consequence of filler–polymer interaction. Figures 4 (a)-(c) illustrates the variation of the storage modulus (E'), loss modulus and $\tan \delta$ of the PA 66/NC nanocomposites as a function of temperature respectively. Table 6 reports values of the storage modulus (E'), loss modulus (E''_{max}) and $\tan \delta$ of the PA 66/NC nanocomposites. For the sake of clarity the plot of $\tan \delta$ as a function of temperature for all nanocomposites is shown in Figure 4. The PA 66 showed a loss modulus peak at 66°C that was attributed to the mobility of the resin molecules. Figure 4 shows the nanoclay dependencies of the loss modulus values of the nanocomposites. The polymer chains nearest to the

reinforcing material are tightly bound, and their mobility is highly restricted. Beyond the tightly bound chains remain the loosely bound chains, which are more restricted in mobility than the bulk polymer but not as restricted as the tightly bound chains at the interface. The E'' value corresponding to T_g was higher in the composites than in the PA 66 (Table 6). The interface, which could easily undergo a larger viscous dissipation, is, resulting in a higher loss modulus value. The ratio of the loss modulus to the storage modulus (E''/E'), i.e., $\tan \delta$, was high for the nanocomposites. The plot of $\tan \delta$ as a function of temperature for all composites is shown in Figure 4(c). Incorporation of the nanoclay in the matrix resin restricted the mobility of the resin molecules, increased the storage modulus values, and lowered the viscoelastic lag between the stress and the strain; hence, the $\tan \delta$ values were increased in the nanocomposites [20]. Compared to the unmodified PA 66, the dynamic storage modulus of the nanocomposite

was approximately 38% higher than PA 66. The higher $\tan \delta$ values in the nanocomposites as compared to the neat resin were also due to the fact that there were fewer matrixes by volume to dissipate the vibrational energy [20]. The loss tangent is a sensitive indicator for cross-linking. The observation from Figure 4(c) reveals that the $\tan \delta$ peak corresponding to the values of T_g shifted towards the higher temperature by the addition of crysnanoclay into PA 66 nanocomposites as compared to pristine PA 66. It can be observed that

the $\tan \delta$ peak of the nanocomposite (T_g) shifts to 75 from 63°C for PA 66 and becomes broader compared to that of PA 66. This can be explained by the existence of strong interactions between clay and the PA 66 matrix, which limits the movement of the PA 66 chain segments. The significant enhancement in E' observed for composites with appropriate compatibilisers is ascribed to the nanoscale dispersion of layered clays, which resulted in a higher aspect ratio feature in the reinforcing clays.

Table 6: Results of DMA analysis of PA 66 /NC nanocomposites

NC content in PA 66 (wt. %)	E' (MPa) at 40 °C	E'_{max} (MPa)	$Tan_{max} \delta$
0	765	66	63
3	1155	81	74
5	1230	87	75

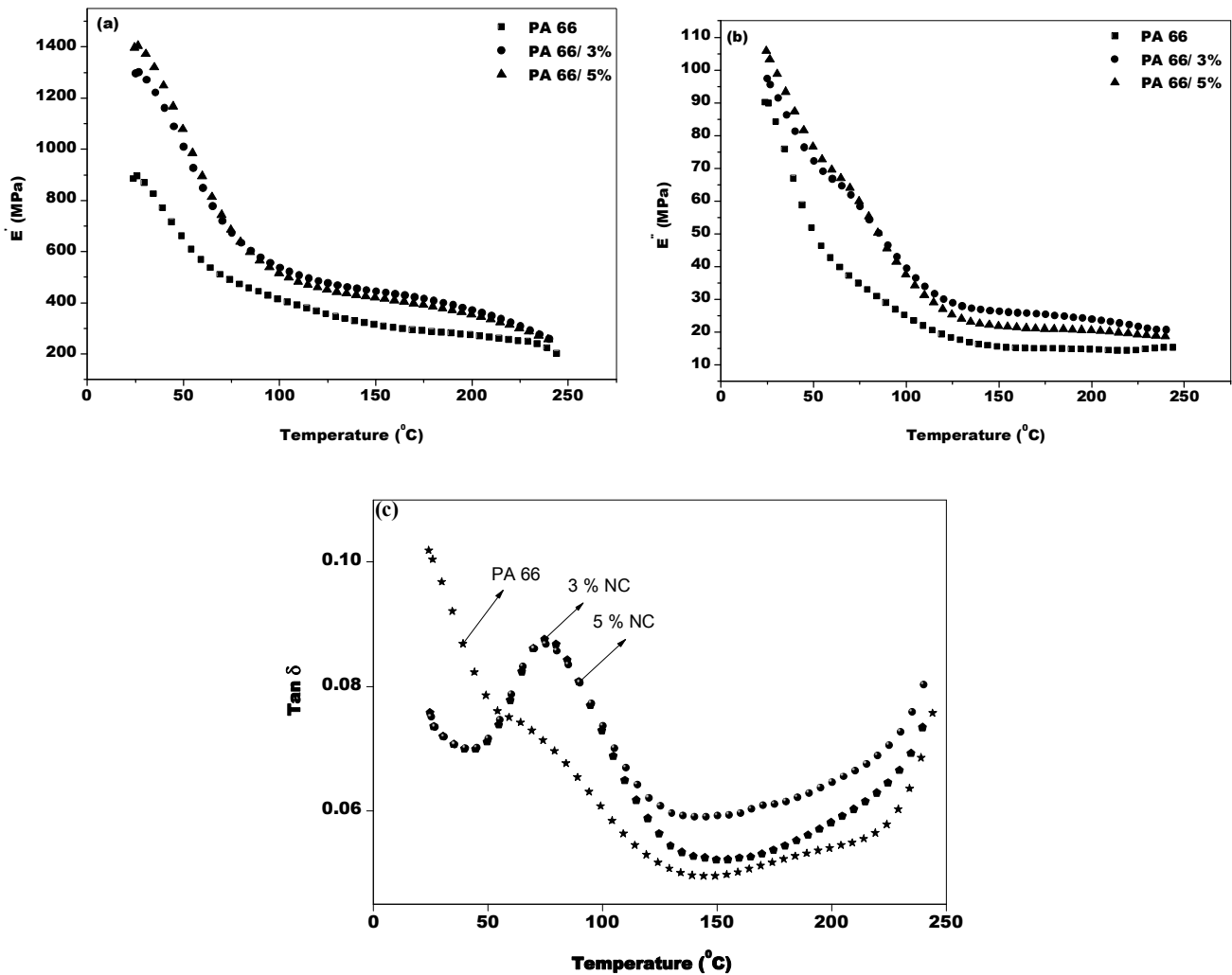


Fig. 4: Plots of (a) storage modulus, (b) loss modulus and (c) Tan δ as functions of temperature of PA 66/CN nanocomposites

Conclusions

PA 66 and PA 66/crysnanoclay were prepared by melt compounding using a twin-screw extruder. In this study; the mechanical properties of nylon 66/crysnanoclay nanocomposites have been evaluated. The effect of clay addition on the hardness, elastic modulus and tensile strength behavior of PA66 and its nanocomposites has been investigated as a function of clay loading. It shows that the hardness and the elastic modulus gradually enhanced with increasing clay concentration. The elastic moduli obtained by nanoindentation are comparable with those obtained from DMA measurements and the tensile tests. The effect of clay concentration on the T_g is significant and complex. The Dynamic mechanical behaviour expectedly observed is closely related to the

physico-mechanical changes occurring upon incorporating nanoclay into the matrix. TGA thermograms indicates that all PA 66 nanocomposites are stable upto 359 °C and undergo one step thermal degradation in the temperature range 359-509°C. Kinetic parameters of thermal degradation were evaluated by using Horowitz–Metzger, Coats-Redfern and Broido's methods. Introduction of the nanoclay (inorganic) phase into PA 66 matrix increases the thermal stability significantly, 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.

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