Preparation of organo nanoclay incorporated polyamide/ melamine cyanurate/nanoclay composites and study on thermal and mechanical behaviours

Shahryar Pashaei[a], Soleyman Hosseinzadeh[b], *

[a]Department of Chemistry, Payame Noor University, P.O. BOX 19395-3697 Tehran, Iran

[b]Department of Chemical Engineering, Payame Noor University, P.O. BOX 19395-3697 Tehran, Iran

Abstract

A series of nylon 66/MCA/NC nanocomposites has been prepared *via* melt compounding by twin screw extruder. A synergistic effect of flame retardant systems based on melamine cyanurate and zinc borate on the flammability and mechanical behaviours of crysnanoclay reinforced nylon 66 nanocomposites have been reported. The physico-mechanical properties such as density, surface hardness and tensile behaviours of PA 66/MCA/CN nanocomposites were investigated by universal testing machine (UTM). Thermal degradation of perisen nylon and nanocomposites was studied by thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). TGA thermograms indicate a significant increase in thermal stability after incorporation of flame retardants additives to nylon 66 matrices. The effect of crysnanoclay on the storage modulus (E), loss modulus (E), and damping factor (tan $_\delta$) as a function of temperature have been measured by dynamic mechanical analysis (DMA). The storage moduli of nanocomposites has been increased after incorporating crysnanoclay in polymer matrix.

Keywords: nylon 66; nanocomposites; flame retardant; mechanical performance; thermal degradation.

*Corresponding author: Soleyman Hosseinzadeh

Tel: +98 (914) 1672215, Fax: +98 (044) 33859003

E-mail: hosseinzadeh65@gmail.com

Introduction

The use of polymeric materials in commercial products has grown substantially, over the last several decades. Polymers are easily processable into a wide variety of shapes and are used to create a composite with properties that are unattainable by the polymer itself. Polymer-clay nanocomposites (PCN) are emerging as a new class of industrially important materials. At loading levels of 2-7 wt%, they offer similar performance to conventional polymeric composites with 30-50 wt% of reinforcing material. High filler loading in the latter materials causes undesirable increase of density, higher melt viscosity and brittleness. Furthermore, the classical composites are opaque with often poor surface finish. These problems are insignificant in PCN [1]. The first results obtained by Toyota Research[1],in the 90s, on the dispersion of nanoscopic platelet silicates (montmorillonite, MMT) in a polyamide 6 matrix have induced considerable worldwide research in the field of nanocomposites consisting of a thermoplastics and clay platelet reinforcement[2–4]. Nylon 66 is a versatile engineering plastic; the successful development of nylon 6 nanocomposites inspired us to study nylon 66/montmoriilonite 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 main objective is a better understanding of the effect of the nanoscopic reinforcements on the mechanical behavior: Young's modulus and yield stress. We first describe the studied material, a polypropylene matrix (PP) reinforced by nanoscopic clay platelets (Montmorillonite, MMT) [6]. Many researchers have characterized the PU composites using thermogravimetric analyzer (TGA) techniques to be familiar with the thermal stability and kinetics of thermal degradation [7]. 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 nylon6/clay nanocomposites [8]. Research on nylon 66/clay nanocomposites was mainly focused on the crystallization and phase transition behaviour of nylon 66 with

inclusions [9,10]. A main objective of the present study is to explore nylon 66/MCA/NC nanocomposites prepared by melt compounding and also investigate the thermal stability and mechanical properties of nanocomposites with (MCA) and varying clay content.

Experimental

Materials

Polyamide 66 (PA66) pellets (Brand name: EPR32, with relative viscosity of 3.2) was obtained from GSRC India. The Crysnano 1030 is a natural montmorillonite mineral modified with quaternary ammonium salt. The typical properties of Crysnano 1030 are d-value – 19 nm at 25 ^{o}C and specific gravity - 1.97 at 25 ^{o}C. The organoamine flame retardant is a multicomponent, synergistic mixture of melamine cyanurate and zinc borate. Compositions and designations of the studied materials are listed in Table 1. Melamine cyanurate (MCA), zinc borate was obtained from GSRC India.

Table 1. Composition of the studied materials in wt%

Material designation	Melamine cyanurate	ZnB_2O_3	Crysnanoclay
A	-	2	-
B	20	2	3
C	20	2	5
D	-	2	3
E	-	2	5

Preparation of nanocomposites

Nylon 66 pellets, crysnanoclay and melamine pellets were oven-dried at 85 °C for 24 h. Then the desired proportions 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 MCA treated PA66 was carried out by Drum

tumliy. Melt blending in a Brabender at a speed of 40 rpm at 280 °C for 5 min. In the case of preparing MCA-treated PA66 with clay, the addition of the materials to the Brabender was in the following sequence: Adding clay to the PA 66 melt mixing for two minutes at 280 °C; adding the additive of MCA, and continuing to mix for three more minutes.

Characterization

The prepared PA 66/MCA/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 PA 66/MCA/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 900 °C in nitrogen gas purge. The oxidation index (OI) was calculated based on the weight of carbonaceous char as related by the empirical equation;

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

The storage modulus ($E^{'}$) and the mechanical loss factor (Tan $= E^{''}/E^{'}$), 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 30-260 °C.

Results and discussion

Physico-mechanical properties of the nanocomposites

The measured physico-mechanical properties such as density, surface hardness and tensile behaviours of PA 66/MCA/CN nanocomposites are nominated in Table 2. It is clear from Table 2 that pristine nylon 66 cast had an average density of 1.122 g/cc. After incorporating flame retardant melamine

(MCA) and 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), Zinc borate (2.7 g/cc) and flame retardant (1.7 g/cc) in low dense polyamide matrix. The density value of the composites lies in the range 1.122 – 1.341 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 melamine cyanurate and nanocrystal into nylon 66 matrix was noticed. The nanocrystal effectively restricts the indentation and increases the hardness of the composites [11].

The impact strength of pristine nylon 66 is 49 J/m and improvement in impact strength was noticed after incorporation of flame retardant additives and crysnanoclay. A drastic improvement obtained in impact strength after corporation of flame retardant into nylon 66. Furthermore, flame retardant loaded PA 66 composites exhibited higher impact strength values was compared to nanoclay loaded PA 66 composites. The impact strength improved 36% after incorporating melamine cyanurate and crysnanoclay into matrix polymer.

The tensile behavior is almost in agreement with earlier reinforced thermoplastic studies [12]. The effects of clay and MCA additives on the mechanical properties are shown in Table 2. The value of the modulus of the composites increases with the weight percentage of clay and MCA additives, indicating a good dispersion of clay in the polymer. Both the Young's modulus of the composites increases with clay content. It is noteworthy that tensile modulus increased by 60% and tensile strength 8 % with the addition of 20 wt% flame retardant and 5wt% clay to PA 66 and tensile modulus increased by 29% and tensile strength 11% with the addition of 5wt% clay into PA66 which is consistent with Kojima's finding [13] on nylon 6/clay nanocomposites. The role of clay as a reinforcing agent in PA 66 matrix is clearly manifested. However, elongation-at-break seems to decrease with composition of nanoclay and MCA additive. The elongation at break of the nanocomposites decreases from about 74% for wth addition 20 wt% of melamine cyanurate and 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 nancomposites increases after incorporating crysnanoclay into matrix polymer. Heat distortion temperatures of PA 66, PA 66/MCN/5% CN, PA 66/MCA/3% CN, PA 66/3% CN and PA 66/5% CN are 200 °C, 275 °C, 270 °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 2. Mechanical properties of nylon 66/MCA/NC nanocomposites

Sample code	Density (g/cc)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Izod impact notched	HDT 0.45 MPa	Surface hardener Shore D (± 2)
A	1.122	2734	78	9.15	49	200	63
B	1.338	6528	83	2.1	74	270	64
C	1.341	6862	85	2.3	76	275	66
D	1.136	3576	85	2.90	51	235	66
E	1.138	3869	88	3.39	68	245	67

Thermogravimetric analysis

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 NC, MCA filled nylon 66 composites are shown in Figure 1 (**a-e**) and TGA thermogram for all the samples is shown in Figure 2. The nylon 66/MCA/CN and nylon 66/CN nanocomposites were stable up to 372 °C.

Tables 3 and 4 corroborated with the results presented in Figures 1 and 2, respectively. The decomposition of pristine PA66 (Figure 1**a** and Table 3) occurs in the range of 372- 506 °C with one DTG peak at 463 °C. The thermal degradation of nylon

66/MCA/5% CN occurred in the temperature range 292-385 °C and 385–518 °C, for first and second steps, respectively. When comparing the TGA and DTG scans for PA 66, PA 66 plus CN with and without MCA (Figure1. (**a-e**) respectively), it is evident that the addition of MCA and or clay does not have a significant effect on the onset temperature of the decomposition of PA66. It is obtained from the Figure 1 (**a-e**) that there is two DTG for PA 66/MCA/CN due to presence of melamine cyanurate beginning at

289 °C reaching a maximum at 385 °C, expected, the amount of ash content of nanocrystal and melamine cyanurate filled polyamide composites lies in the range 1.04-3.86 % (Table 3). It appears that PA 66 with 20 wt% MCA and plus 5% NC begin to decompose earlier than pristine PA 66 due to the decomposition of MCA and the surfactants in crysnanoclay. For second DTG, with addition MCA and NC temperature weight-loss slightly increases from 463 °C to 468 °C.
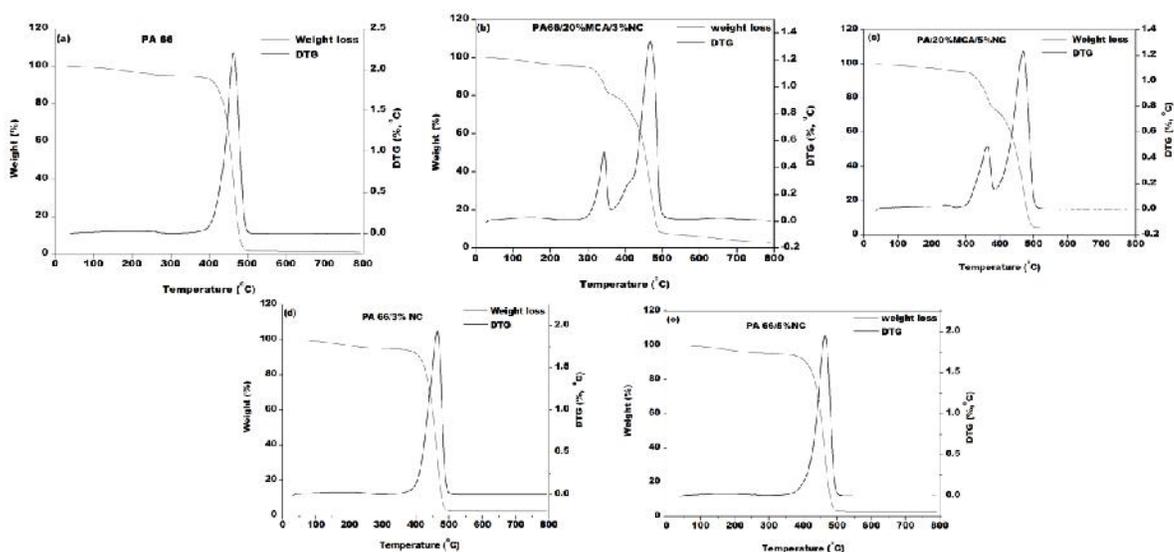

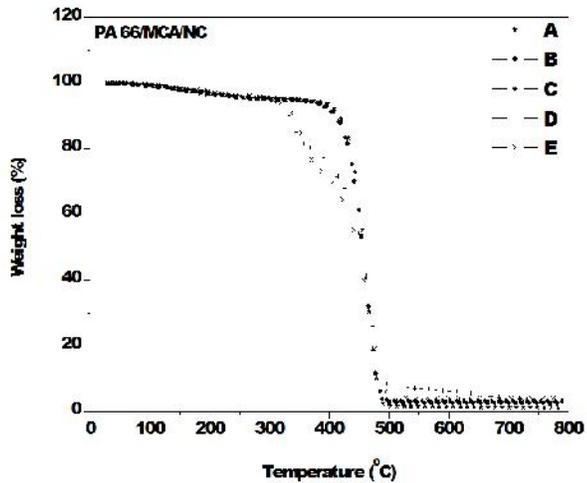**Figure 1.** TGA and derivative thermograms sample code of nylon 66/ MCA/NC nanocomposites

Figure 2. TGA thermograms of sample code nylon 66/ MCA/NC nanocomposites

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

Sample code	Degradation stage	Temperature range ($^\bullet$) ±2			Weight loss (%)
		T_0	T_p	T_c	
A	I	372	463	506	98.96
	Ash	-	-	-	1.04
B	I	289	345	384	4.7
	II	384	468	515	95.3
	Ash	-	-	-	2.93
C	I	292	362	385	2.9
	II	385	470	518	97.1
	Ash	-	-	-	3.86
D	I	374	465	508	97.6
	Ash	-	-	-	2.4
E	I	376	466	509	97.02
	Ash	-	-	-	2.98

TGA data relating to the temperatures corresponding to initial 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 PA 66 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 composites

[14]. It was observed from the table that the PA 66/CN value is more than all compositions (Table 4). It was observed from the Table 4 that the oxidation index values of composites are higher than PA 66 and it lies in the range 0.02 -1.73.This data indicates that the MCN, and crystal nanoclay 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.

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

Sample code	Temperature at different weight loss (± 4 °C)					IDPT (᛫) ±2	Oxidation Index (OI)
	T_0	T_{10}	T_{20}	T_{50}	T_{max}		
A	408	413	437	461	492	411	0.02
B	332	422	444	472	517	500	1.65
C	331	352	408	451	493	484	1.73
D	404	406	433	461	514	421	0.08
E	406	410	433	459	515	423	0.19

Dynamic mechanical analysis (DMA)

The dynamic mechanical thermal analysis (DMA) properties such as loss tangent (tan), loss modulus (E") and storage modulus (E') are recorded as a function of temperature from 0 to 250 °C and showed in Figures 3,

(**a**)-(**c**), respectively. The damping property (tan), as the ratio of the dynamic loss modulus (or viscous) to the dynamic storage modulus (or elastic), is related to the molecular motions and phase transitions. Tan is therefore sensitive to all molecular movement occurring in polymers. For composites, the molecular movement at the interface contributes to the value of tan that enables us to determine the bonding between the interface of the matrix and the filler.

Table 5 reports values of the storage modulus ($E^{'}$), loss modulus ($E^{''}_{max}$) and Tan of the PA 66/MCA/NC nanocomposites. For the sake of clarity, the plot of Tan , as a function of temperature for all nanocomposites, is shown in Figure 3. The PA 66 showed a loss modulus peak at 66 °C that was attributed to the mobility of the resin molecules. Figure 3 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 5). 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 , was high for the nanocomposites. The plot of Tan as a function of temperature for all composites is shown in Figure 3(**c**). It can be noticed from Figure 3 that the incorporation of NC filler to nylon 66 matrix causes remarkable increase of G'' value if the unfilled nylon 66 is taking as reference. This indicates that the addition of rigid filler like NC dissipation of energy also increases. Similar type of observation reported by Hamdan *et al.* for barium ferrite filled thermoplastic natural rubber [15].

Compared to the unmodified PA 66, the dynamic storage modulus of the nanocomposites plus 20% MCA was approximately 48% higher than PA 66. The higher tan 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 [15]. The observation from Figure 3(c) reveals that the tan peak corresponding to the values of T_g shifted towards the higher temperature by the addition of crysnanoclay and MCA into PA 66 nanocomposites as compared to pristine PA 66.

It can be observed that the tan peak of

the nanocomposite (Tg) shifts to 84 °C from 63°C for PA 66 and becomes broader compared to that of PA 66. All the specimens showed a glassy state that is followed by the rubbery state. In general, the storage modulus, E' is found to increase almost linearly with increasing CN content below the glass transition temperature. This indicates that incorporation of the CN filler has improved the stiffness of the PA 66/MCA/CN and the dependence of E' on filler loading is more pronounced around the glassy region. 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 5. Results of DMA analysis of PA 66 /MCA/NC nanocomposites

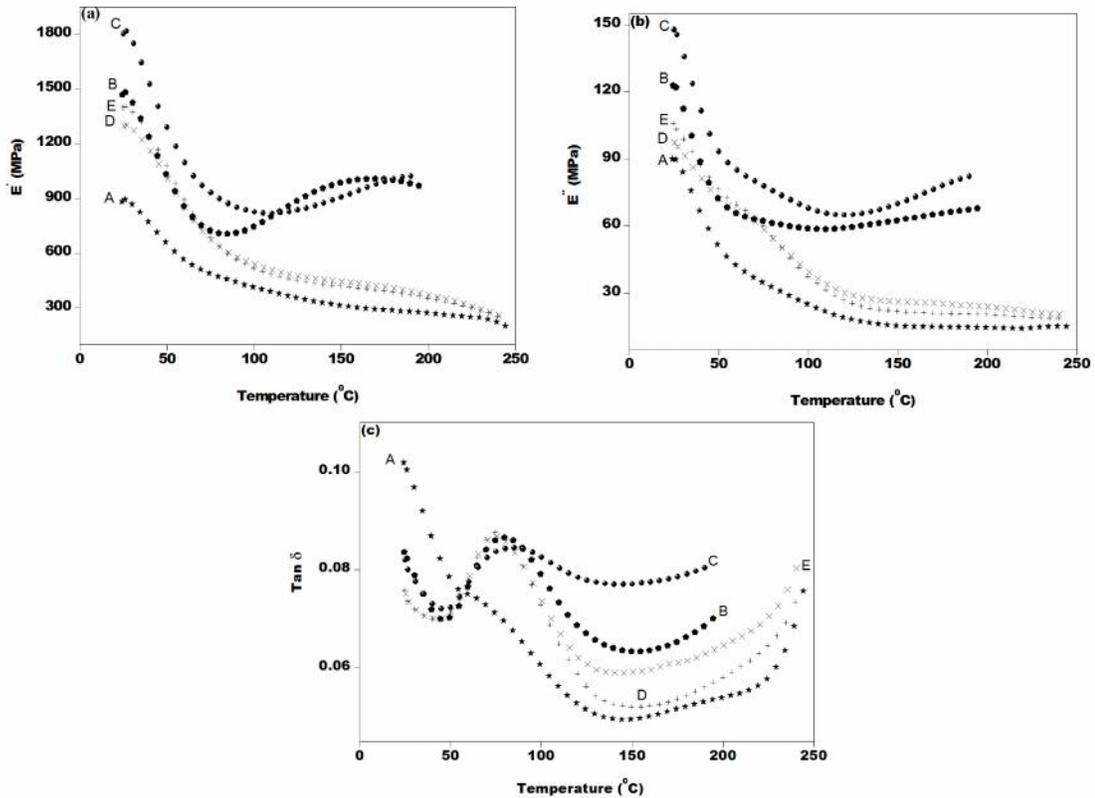| Sample code	E' (MPa) at 40 $^\circ$C	E''_{max} (MPa) at 40 $^\circ$C	Tan_{max} (T_g)
A	776	66	63
B	1237	88	79
C	1510	110	84
D	1152	81	74
E	1237	87	75

Figure 3. Plots of (a) storage modulus, (b) loss modulus and (c) Tan δ as a function of temperature of PA 66/MCA/NC nanocomposites

Conclusion

PA 66 and PA 66/MCA/NC were prepared by melt compounding using a twin-screw extruder. The prepared PA 66/MCA/NC composites show significant improvement in surface hardness, tensile behavior and chemical resistance. The tensile strength of PA 66 composite increased after incorporation of MCA and clay loading. This may be due to good interfacial adhesion of MCA, CN and PA 66 matrix. It was also observed that the

addition of MCA and CN increases the thermal stability of the composites. This may be due to the inorganic nature of MCA and CN filler. The effect of clay concentration on the T_g is significant and complex. The Dynamic mechanical behavior, expectedly observed, is closely related to the physico-mechanical changes occurring upon incorporating MCA and nanoclay into the matrix polymer. TGA thermograms indicates that all PA 66 nanocomposites are stable upto 372 °C

and undergo one step thermal degradation for PA 66 and PA 66/CN in the temperature range 404-515 ^{o}C and two steps thermal degradation for PA66/MCA/NC in the temperature range 284-384 ^{o}C and 384-515 ^{o}C, respectively.

Acknowledgments

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