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THERMAL DEGRADATION KINETICS OF NYLON6/GF/CRYSNANO NANOCLAY NANOCOMPOSITES BY TGA

Nylon 6 is extensively used in engineering applications because of its unique characteristics such as low price, low viscosity, high toughness, shelf lubricating behaviour and high chemical resistance. Nanocomposites based on PA-6 were prepared by melt extrusion and an adjacent injection moulding process. Mechanical and thermomechanical properties have been investigated by tensile testing and dynamic mechanical analysis. To evaluate the potential of crysnano nanoclays as a new candidate in the class of nanofillers, the properties of the crysnano nanoclays nanocomposites has been compared to those of glass fiber. Thermal characteristics were performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). With increase in filler loading, the enthalpy of melting (ΔH_m) obtained from DSC curves was reduced as compared to pristine nylon 6. All the nanocompsoites were stable upto 205 °C. Degradation kinetic parameters have been calculated for thermal degradation processes using the composites using three mathematical models, namely Horowitz-Metzger, Coats-Redfern and Broido's methods.

Key words: nylon 6; crysnano nanoclays; composites; thermogravimetric analysis; thermal degradation behavior; kinetic parameters.

It is known that polymer recycling [1] is increasingly common for two main reasons. The first is economic, mainly in the case of high performance polymers, and leads to the reprocessing of scrap material from transformation processes, such as faulty parts, sprues, runners. The second reason for recycling is environmental, and is due to the increasing amount of post-consumer plastic materials in the waste stream. Polymer recycling is carried out mainly by reprocessing. This involves several high temperature shearing cycles that make easier: *i*) the occurrence of thermal and/or mechanical degradation, *ii*) the consequent chemical and physical changes and *iii*) a detriment of final properties. Therefore, knowing the nature and intensity of the degradation is of interest whether the goal is to choose a stabilizer or to determine the maximum amount of recycled material that may be added to the virgin material without significant losses in the final properties. Polymer nanocomposites are attracting a great deal of attention and have been the focus of study for a large number of research groups. In particular, polymer/layered-inorganic and polymer/clay nanocomposites are being explored extensively due to their high promise for potential applications [2] and as model systems for nanoscopically confined polymers [3]. These polymer/inorganic nanocomposites can be prepared by in situ polymerisation, including solution, suspension, emulsion, and bulk polymerisations, as well as by melt blending and solution mixing [4]. Polymer/clay nanocomposites consist of nanometer-thin clay layers dispersed in a polymer matrix and they exhibit an unusually broad range of properties that are concurrently improved such as mechanical, thermomechanical, barrier, and flame retardancy [5], while maintaining the light-weight character and the optical clarity of the polymer. Since the pristine clays are only miscible with hydrophilic polymers [6], for the vast majority of polymer matrices it is necessary that appropriate surfactants are employed in order to promote interactions that are favourable for mixing between clay and polymer [7]. Despite the low glass transition temperatures (T_g) of these semi-crystalline

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resins, their high crystallinity provides them with a very useful temperature range. Another relatively new development in the field of polymer composites is the introduction of nanocomposites [8], in which small quantities of high modulus nano particles give large improvements in mechanical properties [9]. This can be especially favourable for moisture sensitive polymers like nylons, which lose a lot of their stiffness under moist conditions [10]. The use of nanocomposites as matrix materials in thermoplastic continuous fibre composites is an interesting new option, since the small particles fit easily between the fibres [11] and the increased modulus at temperatures up to the melting point could expand the application window of relatively cheap polymers like polyamides, enabling them to replace more expensive thermoplastic resins in some applications. For most polymers the interaction and exfoliation can be improved by using organic surfactants on the hydrophilic silicate surface as compatibilizer. Since most layered silicate platelets are negatively charged, cationic surfactants such as quaternary ammonium ion based surfactants are often used to optimise the interaction between the platelets and the polymer. The increased stiffness of nanocomposites compared to unfilled polymers might improve the matrix dominated properties of continuous fibre composites, like compressive and flexural strength [12], provided that the interfacial bonding of the fibres with the nanocomposite matrix is not negatively influenced by the addition of the fillers. The present research article deals with the thermal degradation kinetics of nylon6/GF and nylon6/crysnano nanoclay nanocomposites. Degradation kinetic parameters such as energy of activation (E_a) for thermal degradation was calculated for the nanocomposites using three mathematical models, namely Horowitz-Metzger [13], Coats-Redfern [14] and Broido's [15] methods and the results are compared.

EXPERIMENTAL

Materials

Polyamide 6 (PA6) with a trade name of Gujlaiuine IZ-28 was obtained from GSRC, India. The crysnano 1030 is a natural montmorillonite mineral modified with quaternary ammonium salt. The typical properties of crysnano 1030, is d-value - 19 at 25 °C and specific gravity - 1.97 at 25 °C. Specimens for tensile and thermal testing were produced by a lab-scale injection moulding device (DSM micro-injector) with barrel and mould temperatures of 240 and 80 °C.

Preparation of composites

Nylon 6 pellets, crysnano nanoclay and glass fiber 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 210-245 °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 240 °C nozzle and 60 °C, respectively. A series of preparation of crysnano nanoclay and glass fiber treated PA6, was carried out by Drum tumliy. Melt blending was performed in a Brabender at a speed of 40 rpm at 240 °C for 5 min.

Techniques

The prepared polyamide/GF and polyamide/crysnano 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 transition temperatures 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 dynamic DSC 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 polyamide/GF and polyamide/NC nanocomposites has been evaluated using DuPont TGA 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 nylon6/NC and nylon6/GF nanocom-

posites using Horowitz-Metzger [13], Coats-Redfern [14] and Broido's [15] 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) [13] relation used to evaluate the degradation kinetics is:

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

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. The plot of ln [-ln (1 - α)] *versus* θ should give a straight line whose slope is E_a/RT_s^2. Coats-Redfern (CR) [14] relation is as follows:

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

where α is the fraction of sample decomposed at 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 - α)/T^2) *versus* 1/T gives the slope for evaluation of the activation energy most appropriately. Mathematical expression of Broido's (BR) [15] method is as follows:

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

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 - α)) *versus* 1/T.

The heat distortion temperature of the specimens was examined by a heat distortion temperature machine (CS-107, Costom Scientific Instruments, USA). Specimens were measured according to ASTM D48--95.

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

The mechanical properties of the PA6 and their composite systems

The measured physico-mechanical properties such as density, surface hardness and tensile behaviors of nylon6 composites are nominated in Tables 1 and 2. From Table 1 it is clear that nylon6 cast had an average density of 1.13 g/cm^3. After incorporating glass fiber and 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 glass fiber (2.5 g/cm^3) and nanofiller (1.97 g/cm^3) in low dense polyamide matrix. The density values of the composites increases with increase in filler content and it lies in the range 1.13-1.138 g/cm^3. It was 1.265 g/cm^3 for nylon6/GF.

The composites in this investigation consist of three components, namely the matrix, nanoclay and glass fiber. The theoretical density of composites in terms of weight fraction can easily be obtained as per the following equation [16]:

Table 1. Mechanical properties of nylon 6/GF and nylon6/crysnano nanocomposites

GF/NC content in nylon 6, mass%	Density, g/cm^3		Void content	Tensile modulus	Tensile strength	Elongation at break
	Experimental	Theoretic	%	MPa	MPa	%
PA6	1.13	-	-	2415	75	15.4
PA6/GF	1.265	1.404	9.9	5353	124	4.93
PA6/ NC 3%	1.136	1.155	1.6	3545	83	15.01
PA6/NC 5%	1.138	1.172	2.9	4150	88	15.15

Table 2. Influence of crysnano clay content and glass fiber on physic- properties and water uptake of nylon6 nanocomposites

GF/NC content in nylon 6, mass%	Izod impact strength, J/m	HDT at 0.45 °C	Surface hardness shore D (±)	Water uptake, %
PA6	28	180	50	0.03
PA6/GF	75	207	63	0.018
PA6/3%	68	188	62	0.025
PA/5%	120	191	63	0.021

$$P_{ct} = \frac{1}{\left(\frac{W_s}{P_s}\right) + \left(\frac{W_m}{P_m}\right) + \left(\frac{W_p}{P_p}\right)} \quad (5)$$

where W and P represent the weight fraction and density, respectively. The suffixes s, m and ct stand for the nanoclay, matrix and the composite materials, respectively. The suffix p indicates the particulate filler materials. The actual density (P_{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:

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

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 glass fiber as reinforcement and crysnano nanoclay as nanofiller, more voids are found in the composites. The calculated void content of the composites lies in the range 1.6-2.9%. As the filler content increases from 3 to 5 mass% 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 [16]. 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.

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 50 to 63 shore D with increase in crysnano nanoclay content and glass fiber were noticed (Table 2). The crysnano filler effectively restrict the indentation and increases the hardness of the composites [17].

Mechanical properties of composites 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 in the matrix. It was noticed from the data in Table 1 that much higher values of tensile strength were obtained than those of nylon6. Tensile strength at break of nylon6/GF and nylon6/NC composites markedly increased from 75 to 124 MPa and from 75 to 88 MPa, respectively, with an increase in crysnano nanoclay content, which is surprising, considering micro-scale dispersion of clay particles and polymer - filler tethering. The elongation at break of nylon6/GF much lower than nylon6. The elongation at break of nylon6/NC was the same value. Tensile modulus of filled composites were higher than the unfilled polymer (2415 MPa) and among composites tensile moduli increased from 3545 to 4150 MPa with increase in crysnano nanoclay content in nylon6 matrix (Table 1). A similar trend in tensile modulus with increase in filler content has also been reported elsewhere [18]. This improvement in property may be due to the better stress propagation between the composite components. Poorly dispersed fillers can easily agglomerate and obstruct stress propagation. On the other hand, well dispersed fillers prevent the obstruction of stress propagation, thus allowing the stress to be well propagated and restricts the molecular mobility.

The impact strength evaluation is an important parameter to study the toughening behavior of polymer composites. The influence of glass fiber and nanoclay incorporation into nylon6 on the impact strength of nylon6/GF and nylon6/NC composites is shown in Table 2. The impact strength of the composites is higher than nylon6 (28 J/m). From the table it was noticed that a noticeable improvement in impact strength of the composites as increase in crysnano nanoclay in nylon6 matrix.

Water absorption plays a crucial role on properties of nanocomposites. The water uptakes of crysnano clay filled nylon 6 composites with various concentration of nanoclay are shown in Table 2. Water absorption of nylon 6 was 0.03 mass% and for nanocomposites it lies in the range 0.018-0.25 mass% (Table 2). From the table it was noticed that lower water uptake behavior for composites as compared to nylon 6. This result indicates that nanocomposites are resistive to water. However, a slight increase in water uptake behavior with duration of exposure was noticed. Furthermore, as increase in nanoclay content in nylon 6, the composites becoming more resistive towards water.

Heat distortion temperature (HDT) of a polymeric material is an index of heat resistance towards applied load. From Table 2 showed that the HDT of nylon6 increases from 180 to 207 °C for nylon6/GF. In nylon6/NC nanocomposites, there is an increase in HDT from 180 °C for the neat nylon6 to 191 °C for 5 mass% nanocomposite, due to the increase in degree of crystallinity of nylon6 nanocomposites and the presence of strong hydrogen bonds between the matrix and crysnano nanoclay surface.

Thermal analysis

Thermogravimetric analysis

TGA has proved to be a suitable method to investigate the thermal stability of polymeric systems. Thermal degradation and mode of decomposition under the influence of heat is highly recommended for the optimization of process parameters. The nylon6/GF and nylon6/NC nanocomposites were stable up to 387 °C. The threshed decomposition temperature gives an indication of the highest processing temperature that can be adopted.

The TGA thermograms of nylon6 and nylon6 composites are shown in Figures 1a and 1d, respectively along with derivative thermograms. TGA thermograms of all polyamide nanocomposites are shown in Figure 2. Tables 3 and 4 corroborated with the results presented in Figures 1 and 2, respectively. The decomposition of pristine PA6 (Figure 1a and Table 5) occurs in the range of 345-511 °C with one DTG peak at 472 °C. The thermal degradation of nylon6/GF occurred in the temperature range 346-513 °C, with one DTG peak at 475 °C. PA6 does not leave any residue. The addition of 3 and 5 mass% nanocrystal increases the residue to 1.14 and 2.69% and do not significantly change the thermal analysis of the system. The ash content of nanocrystal and glass fiber filled polyamide composites lies in the range 1.14-26.10%, where the ash content of PA6/GF is higher than for all other compositions (Table 5).

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}

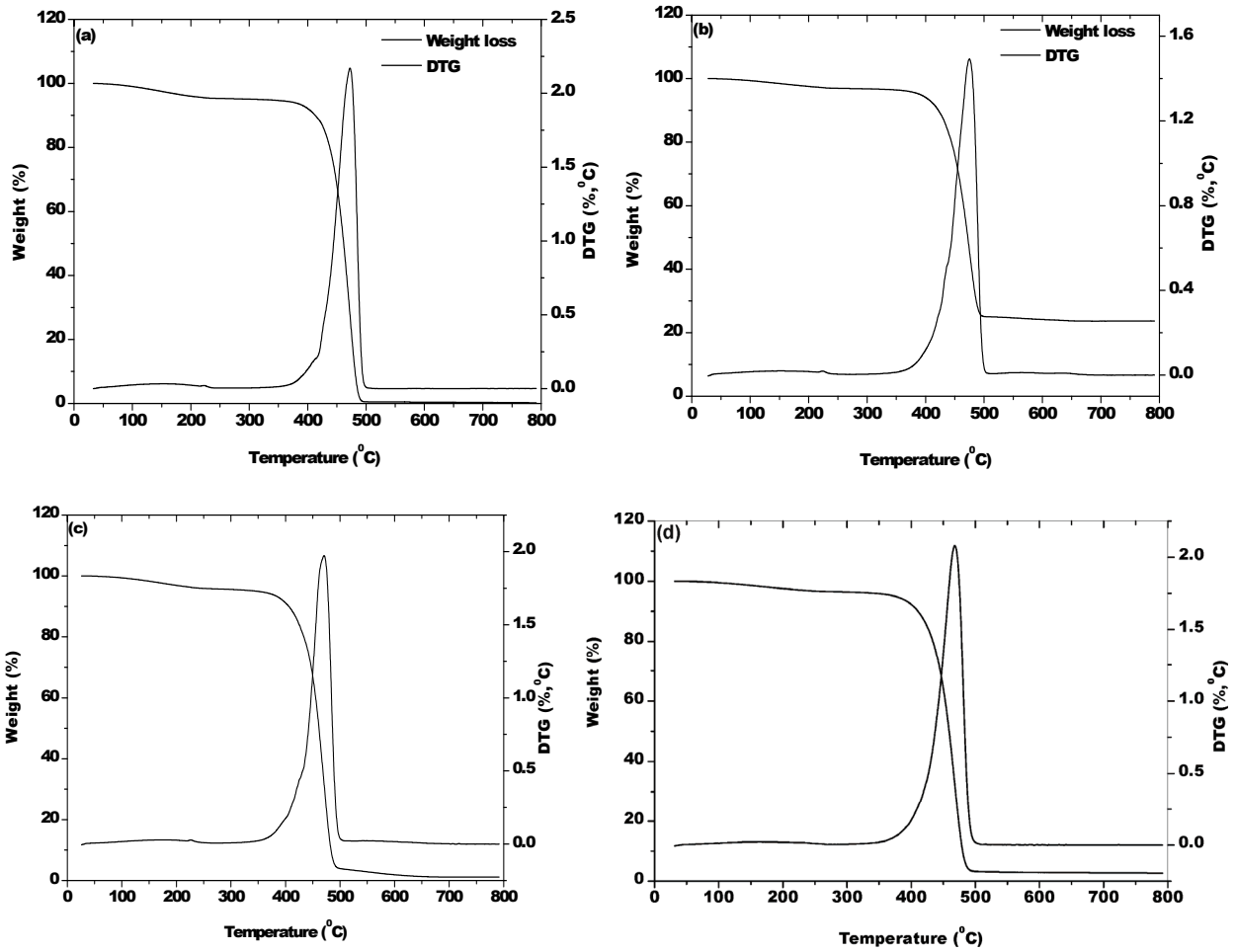

Figure 1. TGA and derivative thermograms of a) PA6, b) PA6/GF, c) PA6/NC 3% and d) PA6/NC 5% polyamide nanocomposites.

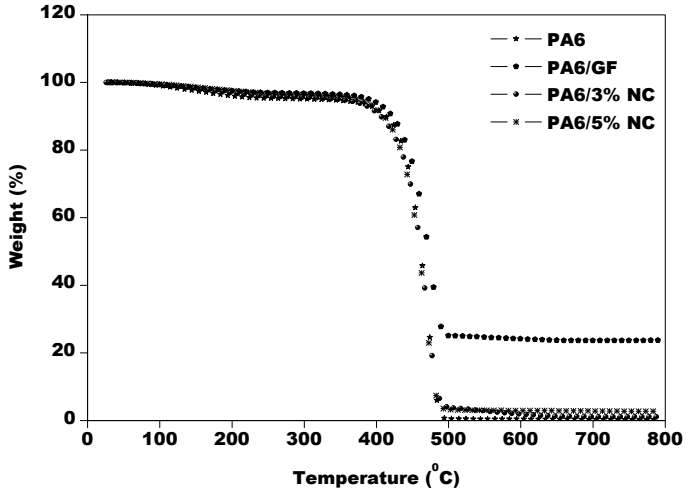

Figure 2. TGA thermograms of nylon6 and polyamide composites.

Table 3. Thermal data obtained from TGA thermograms of nylon 6/GF and nylon6/crysnano nanocomposites

GF/NC content in nylon 6, mass%	Temperature at different weight loss, °C (±4 °C)					IDPT, °C (±2 °C)	Oxidation index (*OI*)
	T_0	T_{10}	T_{20}	T_{50}	T_{max}		
PA6	391	413	437	461	492	411	0.02
PA/GF	405	422	444	472	517	500	1.65
PA6/ NC 3%	387	406	433	461	514	421	0.08
PA6/NC 5%	392	410	433	459	515	423	0.19

Table 4. Data from DSC thermograms of nylon 6/GF and nylon6/crysnano nanocomposites

GF/NC/MC content in nylon 6, mass%	T_c / °C	T_m / °C	H_m / J g^{-1}	Crystallinity, X_c / %
PA6	211	224	49.4	21.5
PA/GF	209	222	44.7	19.4
PA6/ NC 3%	206	221	46.2	20.1
PA6/NC 5%	205	221	30.8	13.4

Table 5. Thermal degradation temperature range obtained from derivative TGA curves of nylon 6/GF and nylon6/crysnano nanocomposites

GF/NC content in nylon 6, mass%	Temperature, °C (±2 °C)			Ash content, %
	T_0	T_p	T_c	
PA 6	345	472	511	0.2
PA/GF	346	475	513	23.7
PA6/ NC 3%	345	470	505	1.1
PA6/NC 5%	345	468	518	2.7

(temperature for 50% weight loss) and T_{max} (temperature for maximum weight loss) are the main criteria to indicate the thermal stability of the composites. The relative thermal stability of PA6 nanocomposites have been evaluated by comparing the decomposition temperatures at different percentage weight loss (Table 3). The higher the values of T_{10}, T_{20}, T_{50} and T_{max}, the higher the thermal stability of the composites [19]. From the table 3 it was observed that the PA6/GF value is higher than for all other compositions. From Table 3, it can be observed that PA6/GF composites showed which onset degradation values of nylon6/GF are higher than of pristine PA6 and PA6/NC. The higher the values of oxidation index (*OI*), the higher the thermal stability [20]. From the Table 3 it was observed that the oxidation index values of PA6/GF and PA6/NC is higher than PA6 and it lies in the range 0.08-1.65. This data indicates that the glass fiber and

crystal nanoclay filled nylon6 composites are more thermally stable than that of pristine PA6. PA6 composites under investigation do not breakdown 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.

Kinetic analysis of thermal degradation. Kinetic parameters were evaluated from the TGA curves using Horowitz-Metzger, Coats-Redfern and Broido's methods. The plots of ln [-ln (1 - α)]/T^2] *versus* 1/T (CR), ln [-ln (1 - α)] *versus* 1/T (BR) and ln [-ln (1 - α)] *versus* θ (HM) for nylon6 and its nanocomposites are shown in Figures 3a-3c, respectively. The regression

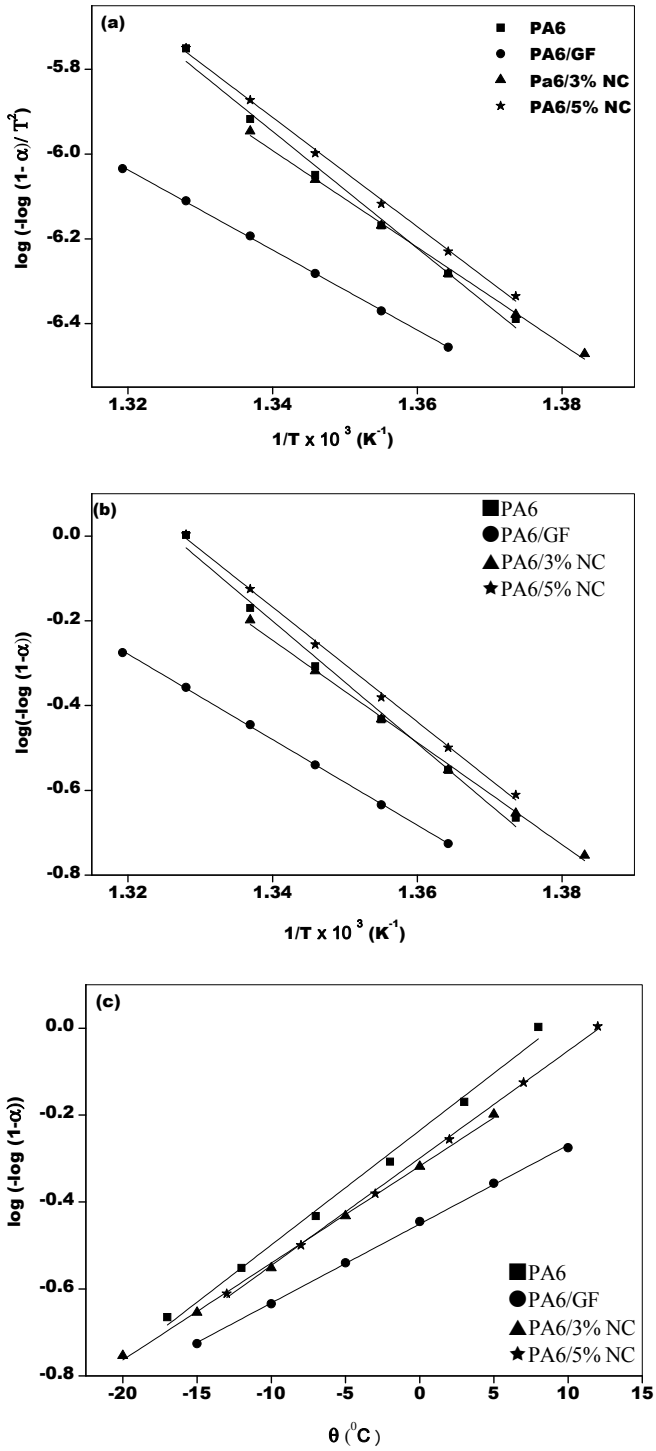

Figure 3. a) Plots of log [-log (1 - α)/T^2] versus 1/T using Coats-Redfern method, b) plots of log [-log (1 - α)] versus 1/T using Broido's method and c) plots of log [-log (1 - α)] versus θ using Horowitz-Metzger method for the determination of activation energies.

analysis gives the slopes, constants and R^2 for each 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 and for each method are tabulated in Table 6.

The E_a values lies in the range 78-100, 181-247 and 193-276 kJ/mol for Horowitz-Metzger, Coats-Redfern and Broido's methods respectively. The lowest E_a value was for unfilled composite as compared to composites. This is due to the lower energy required to remove volatile components and low molecular weight materials present in nylon6 nanocomposites. Lower E_a values were observed for higher nano filler loaded nylon6 composites. This is due to the lower energy required for bond scission and unzipping of nylon6/ /GF and nylon6/NC nanocomposites. The kinetic analysis suggests that an enhanced thermal stability of composite is associated with the increase in the effective activation energy of their degradation process.

Differential scanning calorimetry

DSC was used for characterization of the polymer matrix. The obtained DSC thermograms of neat PA6 and its composites are shown in Figure 4. It in noticed that melting curves of semicrystalline PA6 was not identical to the corresponding crystallization curves. The thermal data obtained from DSC curves of neat PA6 and glass fiber, crystal nanoclay filled composites are summarized in Table 4. There was no significant change in melting temperature (T_m) for pristine polyamide and its composites. The enthalpy of melting (ΔH_m) was highest for pristine PA6 (49.4 J/g) and it was significantly reduced from 49.4 to 30.8 J/g after incorporation of glass fiber and crystal nanoclay. The percent of crystallinity of polyamide also decreased after incorporation of glass fiber and crystal nanoclay.

The values of ΔH_m provide important information about the crystallinity of the composites. Based on the DSC results and considering the proportions, it is possible to draw the following conclusions [21]:

If ΔH_m of the composites is lower than 80% of the value of the pristine polyamide, it means that the loading additive interacted with the polymer decreases its crystallinity.

If ΔH_m of the composites is higher than 80% of the value of the pristine polyamide, it means that the loading additive interacted with the polymer increases its crystallinity.

Table 6. Activation energies calculated by Horowitz-Metzger (HM), Coats-Redfern (CR) and Broido's (BR) methods with the respective concurrency value (R^2) for nylon6 and its composites

GF/NC content in nylon 6, mass%	Activation energy, E_a / kJ mol^{-1} (±4%)					
	HW	R^2	*CR*	R^2	*BR*	R^2
PA6	111	0.994	264	0.992	276	0.992
PA6/GF	78	0.999	181	0.999	193	0.999
PA6/3% NC	93	0.998	219	0.997	231	0.997
PA6/5% NC	100	0.999	247	0.998	259	0.998

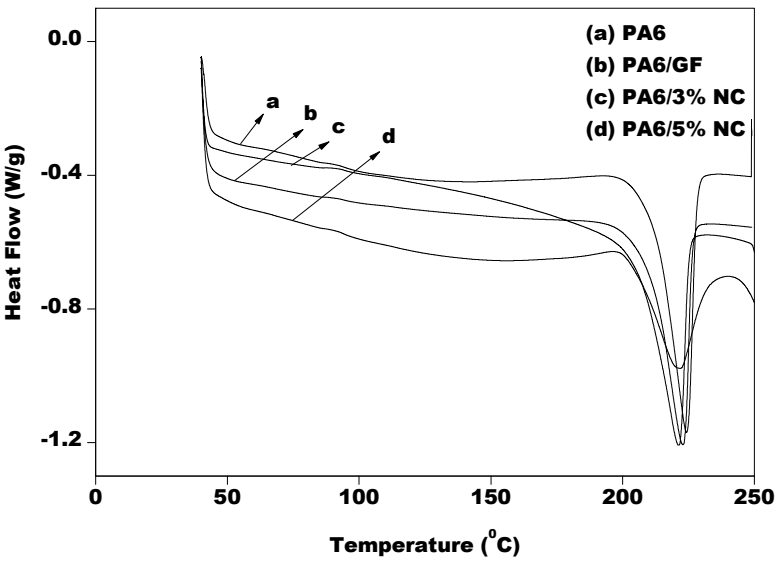

Figure 4. DSC thermograms of pristine nylon 6 and their composites.

If ΔH_m of the composites is 80% of the value of the pristine polyamide, it means that the loading additive does not interact with the polymer.

From the results obtained for ΔH_m (Table 4), it is observed that PA6 has higher ΔH_m value. The crystallinity values for the composites were calculated using the ΔH_m value of 100% crystalline polyamide (230 J/g) [22].

Dynamic mechanical analysis (DMA)

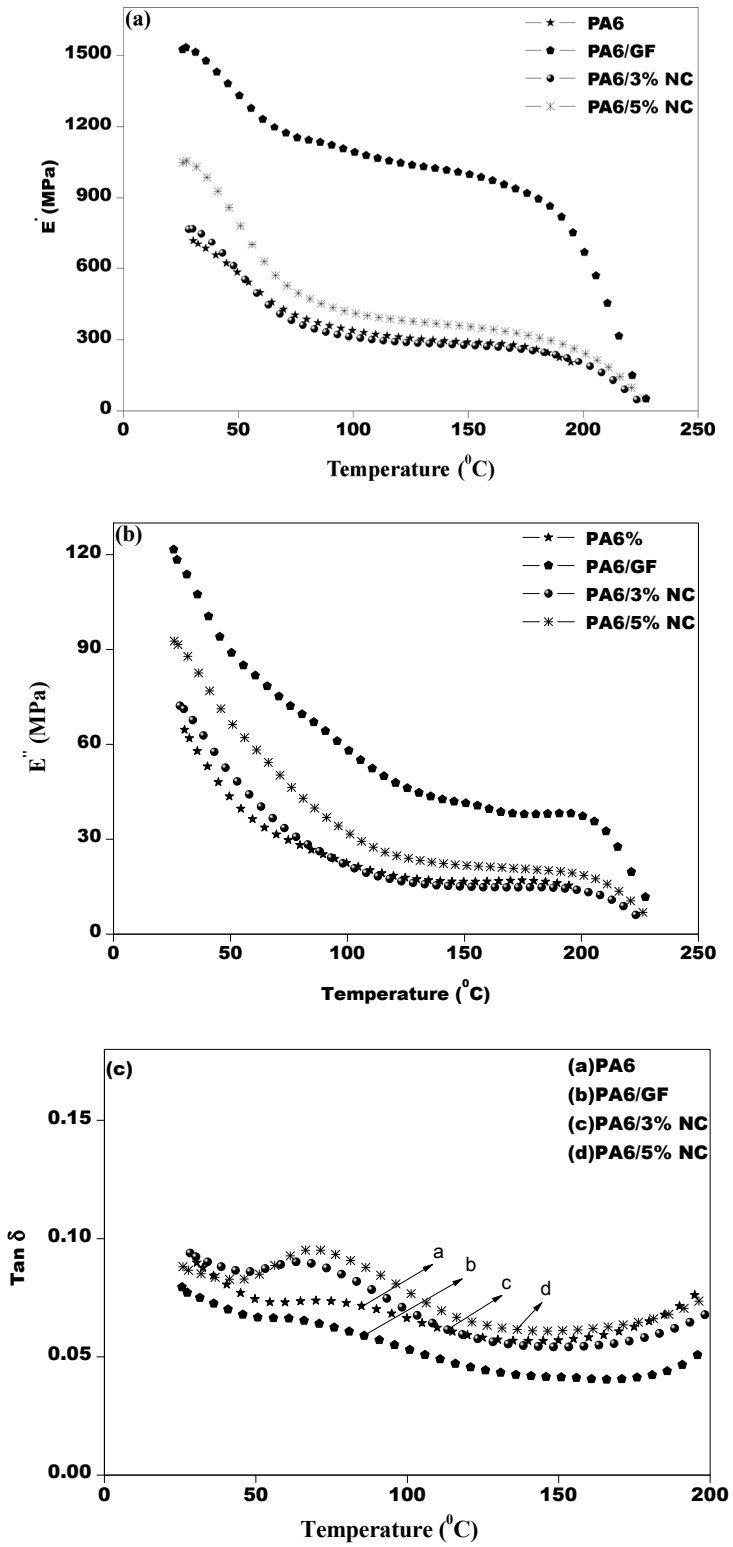

Figure 5. Plots of a) storage modulus, b) loss modulus and c) tan δ as a function of temperature of nylon 6 composites.

Dynamic mechanical analysis (DMA) is a very sensitive technique which permits determination of the viscoelastic behaviour of polymers and provides valuable insights into the relationship between structure, morphology and properties of composite materials. The variations of E' and tan δ observed for the different systems are plotted in Figure 5. In DMA, the loss factor (tan $\delta = E''/E'$) represents the damping within the material and its evolution can be associated with macroscopic physical transitions. The temperature corresponding to the cooperative a-relaxation, commonly named dynamic glass transition temperature (T_g), has been estimated at the maximum of tan δ peak and the T_g values of each specimen are listed in Table 7.

Table 7. Results of DMA analysis of nylon 6/GF and nylon6/crysnano nanocomposites

GF/NC content in nylon 6, mass%	E' / MPa at 40 °C	E''_{max} / MPa	tan δ_{max}
PA6	652	52	0.073 (70 °C)
PA/GF	1439	101	0.066 (60 °C)
PA6/ NC 3%	703	61	0.09 (64 °C)
PA6/NC 5%	953	78	0.1 (68 °C)

The plots of storage modulus (E'), loss modulus (E'') and tan δ for all composites are shown in Figures 5a-5c, respectively. The effect of glass fiber and crysnano nanoclay on storage modulus, loss modulus and tan δ of nylon6/GF and nylon6/NC nanocomposites can be seen from Table 7, which we list the average values of the storage modulus (E') with glass fiber and crysnano nanoclay. The storage modulus values increased with the addition of 3 and 5 mass% crysnano nanoclay. The E' of nylon 6/GF measured at 40 °C were 1439 MPa, which are higher than other compositions. However, in the case of crysnano filled nylon6 composites, E' increases monotonically with increase in filler content from 3 to 5%. The maximum E' was 1439 MPa for nylon6/GF which is about 55% higher than that of nylon6. Table 7 also lists the average values of T_g for nylon6 and composites. The measured T_g of nylon6 was 70 °C. The effect of glass fiber and crysnano nanoclay on E'' and T_g can be noticed in Table 7. For the addition of 3 and 5 mass% crysnano nanoclay, the T_g of nanocomposite was 6 and 2 °C less than that of nylon6, respectively. Tan δ at T_{max} of the nanocomposites was in general higher than that of matrix polymer, and it increased as the percentage weight of MMT increased. This increase in the damping factor was attributed to the exfoliated of nylon6 by MMT, which caused increase in the matrix viscoelasticity. Various mechanisms like matrix viscoelasticity, filler/filler interfacial friction, etc., could increase the damping capacity of the polymer composite materials.

CONCLUSIONS

The tensile strength of nylon 6 containing 20 mass% glass fiber is 40% higher than that of nylon 6, while the tensile modulus of PA6/GF increases by 55% and tensile strength of nylon 6/clay is 12% higher than that of neat nylon 6, while the tensile modulus of PA6/clay increases by 32%. Heat distortion temperatures of nylon 6 and nylon 6/GF are 180 and 207 °C, respectively. Consequently, the heat distortion temperature of nylon 6/NC system is almost 10 °C higher than that of neat nylon 6. Notched izod impact strength of the composites increased with the addition of the glass fiber and crysnano nanoclay. The thermal stability and degradation kinetics of nylon 6 and its nanocomposites have been reported in this research investigation. TGA thermograms indicates that all nylon 6 nanocomposites are stable upto 387 °C and undergo thermal degradation in the temperature ranges 345-511, 346-513, 345-505 and 345-518 °C, respectively. It can be observed that the thermal stability of the glass fiber and crysnano nanoclay loaded nylon 6 composites is as same as compared to nylon 6. Kinetic parameters of degradation were evaluated by using Horowitz-Metzger, Coats-Redfern and Broido methods. Introduction of the glass fiber and crysnano nanoclay phase into nylon 6 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 all the three methods is comparable. Lowest activation energy values were observed for nylon 6/GF and 3 mass% of nanocomposites for thermal degradation process as compared to neat nylon 6. The kinetic analysis suggests that the enhanced thermal stability of nanocomposites is associated with the increase of the effective activation energy of their degradation. The storage modulus values increased with the addition of 3 and 5 mass% crysnano nanoclay. The E' of nylon 6/GF are higher than all compositions.

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NAUČNI RAD

ISPITIVANJE KINETIKE TERMALNE DEGRADACIJE NANOKOMPOZITA NA BAZI NYLON6/GF/CRYSNANO NANOGLINE POMOĆU TGA

Nylon 6 ima široku primenu u inženjerstvu zbog svojih specifičnih karakteristika kao što su: niska cena koštanja, mala viskoznost, velika čvrstoća, lubrifikacione osobine i visoka hemijska otpornost. Nanokompoziti su pripremljeni ekstruzijom otopljenog polimera i brizganjem. Proučavane su mehaničke i termomehaničke karakteristike ispitivanjem čvrstoće i dinamičkom mehaničkom analizom. Kako bi se ispitala mogućnost primene nanogline Crysnano kao nanopunioca, karakteristike nanokompozita na bazi ove nanogline su poređene sa staklenim vlaknima. Termalne karakteristike su ispitane pomoću termogravimetrijske analize (TGA), diferencijalne scanning kalorimetrije (DSC) i dinamičke mehaničke analize (DMA). Rezultati dobijeni pomoću DSC krive pokazuju da se sa povećanjem punioca entalpija topljenja (ΔH_m) smanjuje u poređenju sa nekadašnjim naylon 6. Svi nanokompoziti su stabilni do 205 °C. Kinetički parametri degradacije su određeni pomoću procesa termičke degradacije kompozita, korišćenjem matematičkih modela Horowitz-Metzgera, Coats-Redferna i Broidoa.

Ključne reči: nylon 6; crysnano nanogline; kompoziti; TGA; termička razgradnja; kinetički parametri.