

Studies on Fabrication and Characterization of Nanoclay Reinforced Nylon-6 composites: Enhancement of Heat distortion Temperature

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Abstract

Organically modified nanoclay (cation exchange capacity of 135 to 145 meq/100g) was used as nanophase reinforcement for fabrication of nylon-6 nanocomposites. The thickness of clay platelets varied from 1.2 nm to 1.3 nm with 3.485 nm as d-spacing. Nylon 6/nanoclay composites were fabricated with loading of 2.5, 5.0 and 10 wt. % nanoclay via direct melt compounding technique using conventional twin-screw extruder. Processing temperature profile from hopper to header was 230-240-245-260 °C and screw speed was maintained at 180 rpm. The nylon 6/clay nanocomposites were characterized for thermal and mechanical properties. The structural properties were characterized by Differential Scanning Calorimeter (DSC) and X-ray diffraction analysis. The tensile fracture morphology was analyzed by using Scanning Electron Microscope (SEM). DSC nonisothermal curves show an increase in the crystallization temperature with increasing degree of crystallinity. The crystallization rate of the nanoclay reinforced nylon 6 composites was found to be significantly faster than that for the pristine nylon 6 and suggests that the layered silicates act as nucleating centers. XRD result shows that addition of nanoclay by this technique favors the formation of γ -crystalline phase in nylon 6/nanoclay composites. Due to this, there is substantial enhancement in the tensile strength and Izod impact strength. A variation from 700 to 971 Kg/cm² for tensile strength and from 3.0 to 3.4 Kg.cm/cm of notch for Izod impact strength. The detailed results are presented.

Introduction

Nanocomposites refer to composites where one of the components has at least one dimension of the order of a few nanometers. They are a relatively new class of materials. Filled polymers are found in a number of industrial and commercial areas including automotive, electrical, industrial components, power tools, pulley and gears. Using filled polymers, enhancement of physical properties and the addition of filler-specific characteristics as well as reduced resin volume and thus cost. Industrially useful properties include increase of tensile strength up to 25%, flexural modulus up to 100%, and impact strength up to 100% and low shrinkage upon secondary processing and high heat distortion temperature. Polymer-layered silicate nanocomposites challenge traditional filled polymers (loadings of 20 wt % or more) in many of these areas by providing similar physical enhancements but with as little as 5 wt % addition of dispersed, 1 nm thick aluminosilicate layers (diameters of layers commonly ranging from

200-300 nm (Montmorillonite)) [1]. Compared to their micro- and macro counterparts and the net polymer matrix, polymer/clay nanocomposites exhibit improved tensile strength, impact strength, heat distortion temperature (HDT), barrier properties and decrease gas permeability, thermal expansion, flammability [3-7]. Moreover, they can display interesting conductivity properties and improved biodegradability when conductive polymer and biodegradable polymer are involved, resp [8]. The enhanced properties of polymer layer silicate nanocomposites are presumably due to the formed nanoscale structure, the large aspect ratio and large area of the layered silicates, and strong interaction between polymer molecular chains and layered silicates. Aspect ratios of such silicates varies from 100 to 1000, and cation exchange capacities vary from 100–150 meq/100g clay [1].

In this article, we focus on the studies on crystallization behavior of nylon6/clay nanocomposites with loading of nanoclay, thermal properties, mechanical properties and fracture properties of nylon 6/clay nanocomposites and their dependence presence of nanoclay.

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Experimental

Materials

Bentonite was obtained from Aashapuri Chemical Ltd. with a particles size of less than 15 μm . The nylon 6 used in the present work was produced by the GSFC, Vadodara. Before using, nylon 6 was dried under vacuum at 80 $^{\circ}\text{C}$ for 12 h to eliminate the water absorbed during the industrial washing.

Preparation of Organically modified clay

The alkyl ammonium exchanged clay was prepared by the reaction of Octadecylamine, with MMT at concentration of 1.25 CEC i.e. salt to clay mass/mass ratios. The suspensions were shaken/stirred vigorously for different period of time, at 700 c. The suspension was washed by hot dist. water until no chloride ion was detected through the reaction with AgNO_3 solution. The solid was dried. The dried clays were ground with a mortar and pestle, and sieved to collect the particle with $<70\mu$.

Preparation of nylon 6/nanoclay nanocomposites

Nylon 6 nanocomposites with loading of different contents of clay nanoparticles were prepared by melt-compounding technique using a twin screw extruder (Bernstorff, Plasticolor 3000, and Germany).

Studies have demonstrated that melt processing condition play a key role in achieving high level of exfoliation [9]. The melt-compounding was carried out at temperature profile ($^{\circ}\text{C}$) of 230 – 240 – 245 – 260 $^{\circ}\text{C}$. The screw speed was kept at 180 rpm and feeding rate of 1 hr to Yield thick fiber of nanocomposites. The thick fiber was passed through

cold water. It was palletized in small granules. The granules of nylon 6/nanoclay nanocomposites were vacuum dried at 80 $^{\circ}\text{C}$ for 24 hrs. The dried granules were processed by using Injection Molding Machine (Windsor SP 30 DD) to make different shape of standard testing specimens for characterization and tests.

Characterization of nylon 6/nanoclay nanocomposites

The nonisothermal crystallization behavior of nylon 6 and its nanocomposites were studied by using the heating–cooling cycles in the temperature range 25 ~ 290 $^{\circ}\text{C}$ by using Differential Scanning Calorimeter METTLER DSC20. The studies of dispersion of clay layers in nylon 6 and crystallization of nanocomposites were carried out using XRD PHILIPS-X'pert with Cu ($\lambda=1.5417\text{\AA}$) irradiation. Tensile strength of nylon 6 and its nanocomposite were measured by using ASTM D638 method at 50 mm/min cross head speed using INSTRON 4302. The Izod impact strength was measured by using ASTM D256 method. Heat Distortion Temperature of nylon 6 and its nanocomposite were measured through ASTM D648 method using HDT. Morphologies of tensile fracture of the nanocomposites were observed on Scanning Electron Microscopy (SEM: HITACHI S-3000N).

Results and Discussions

Differential Scanning Calorimeter

Heating scans were analyzed for the melting temperature, T_m , heat of fusion, ΔH_m , and the degree of crystallinity, X_c , (Fig.1), The DSC measurements

Table 1.
Thermal properties of nylon 6/organoclay nanocomposites

Nanocomposites	Nanoclay (wt.%)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)	ΔH_m (J·g ⁻¹)	X_c (%)	HDT at 264 psi ($^{\circ}\text{C}$)
Nylon	6	224.75	174.72	50.03	64.8	34.46	60 + 2
N6/Nanoclay	2.5	223.14	190.51	32.63	73.8	39.25	59.9
N6/Nanoclay	5	221.75	190.70	31.05	74.3	39.52	80.6
N6/Nanoclay	10	221.66	191.95	29.71	63.4	33.75	85.9

of nylon 6/nanoclay nanocomposites indicate that the presence of organoclay does not affect the T_g of Nylon6 matrix, which occurs at approximately 53 °C. The DSC Melting peak (T_m) of the nanocomposites occurs at slightly lower temperature than that of the neat nylon 6. Table.1 provides Thermal properties of nylon 6/organoclay nanocomposites. The change in the degree of super cooling (ΔT) indicates changes in degree of crystallization. The degree of crystallization significantly increases for polymer nanocomposites with 2.5 wt % of clay compared to the pure nylon 6. On higher loading to 5.0 wt% the increase in degree of crystallization was found to be gradual. The acceleration of the crystal growth is due to heterogeneous nucleation. The clay initiates the faster formation of nuclei as well as formation of more nuclei. Both of these effects lead to an increase of crystallization rate at the beginning of crystallization.

At latter stages the clay has a decreasing effect on the crystallization rate. It acts as an external barrier since the presence of the clay sheets in the polymer melt suppresses the mobility of the polymer chains. The clay can be seen as walls that can hinder the growth of lamellae. The existence of both accelerating and decelerating effect influences the overall crystallization rate. The purely mechanistic effect of these fillers (nanoclay) on the thermal stability of the polymers can be nicely demonstrated through the nylon 6/nanoclay nanocomposites. In the nylon 6/clay nanocomposites studied in the present work, though the melting temperature does not change markedly from that of the respective neat nylon 6 but there is a marked increase of the HDT, from 60 °C for the neat polymer to 85.9 °C for a 10 wt.% organoclay nanocomposites. This is due to

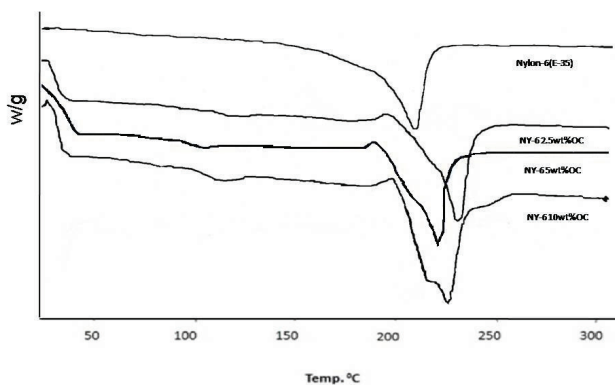


Fig. 1. DSC curves of Nylon-6, Ny-6 2.5wt%OC, Ny-6 5wt%OC, Ny-6 10wt%OC

the presence of strong hydrogen bonds between the matrix and silicate surface.

X-ray Diffractogram

Figure 2 shows the X-ray diffractograms of Organoclay with different CEC concentration and nylon 6 nanocomposites with loading of 10 wt% of organoclay. Montmorillonite consist of tetrahedral silica layer and octahedral alumina layers, carrying negative charge which must be counterbalanced by exchangeable Cation in the interlayer. Such an arrangement results in a basal spacing of around 13.79 Å of the as such bentonite [reference]. This basal spacing depends upon the size of the Cation be it Na^+ , Ca^{+} or Mg^{+} and also on the degree of the hydration of the Cation. Upon the ion exchange of the inorganic Cation by an organic one, the properties of the clay material changes dramatically from a hydrophilic medium to a hydrophobic medium. The basal spacing of OC 1.0 CEC is 19.61 Å, At concentration of 1.5CEC it is increased slightly to 20.66 Å. On higher addition of organic surfactant i.e. 2.0 CEC, the basal spacing reaches highest value 34.88 Å. The expansion of the basal spacing of concentration 2.0CEC is 21.09Å, This value of is about the thickness of the surfactant molecule.

It is clear from above results that the d-spacing of the layer silicate is going to becomes higher and higher on increasing the amount of the surfactant Octadecylamin. Hence such materials have application both in organic media and in water. This ion exchange is dependent on the Cation exchange capacity (CEC) of the Montmorillonite being used.

It indicates that all Nylon 6 Nanocomposites have γ -phase crystalline structure (peak at 21.5°).

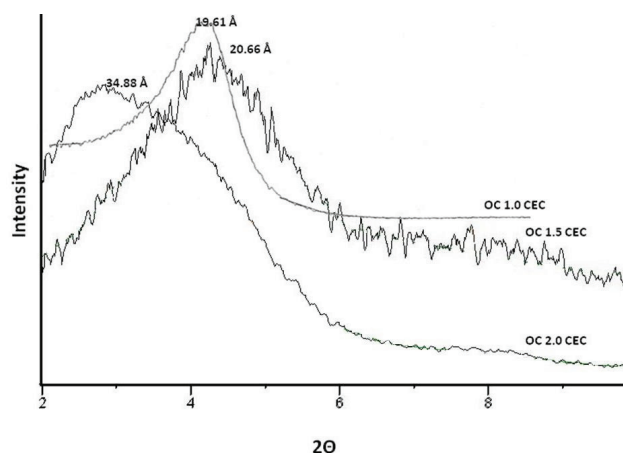


Fig.2 X-ray diffraction patterns of the Oclay 1.0CEC, Oclay 1.5CEC, Oclay 2.0 CEC

Table 2.
Mechanical Properties of Nylon-6/Nanoclay nanocomposite

Sample	Nanoclay in wt %	Tensile strength kg/cm ²	% Elongation	Izod-Impact Test kgcm/cm-notch	HDT (*C)
ASTM Method	--	D638	D638	D256	D648
Nylon-6	0	700+ 50	5	3-4.5	60+ 2
Nylon-6/ Nanoclay	2.5	822.0	47	4.0	59.9
Nylon-6/ Nanoclay	5.0	930	16	5.76	80.6
Nylon-6/Nanoclay	10	971	6	3- 4	85.9

It may be related to the interaction between clay layers and nylon 6 molecules. The addition of clay layers forces the amide groups of nylon 6 out of the plane formed by the chains. This result conformational changes of the chains which limits the formation of hydrogen-bonded sheets and the γ -phase is favored. The increased d-spacing between the clay platelets in nylon 6 matrixes nanocomposite is 20.66 Å. The peak at 4.2° as shown in Figure 1c is indicative

of agglomeration of organoclay in nylon 6 matrix because of large amount of organoclay.

Mechanical Properties

Mechanical properties of Nylon 6/nanoclay Nanocomposites developed in present studies have been compared in Table 2. Recently Nylon-6/clay nanocomposites clearly show better mechanical

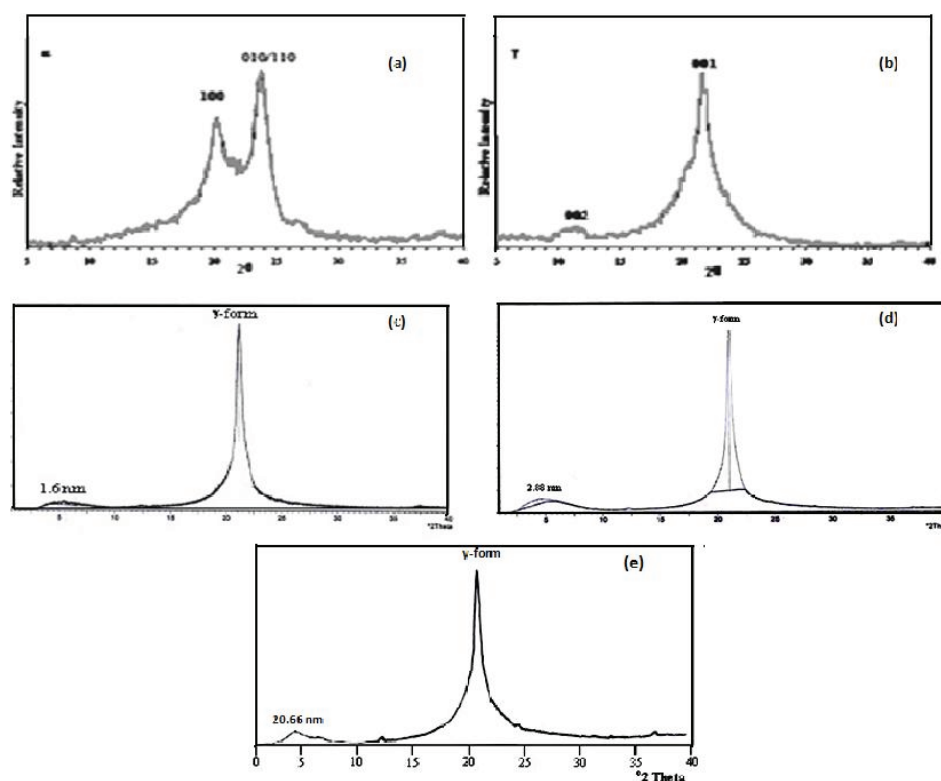


Fig.3 X-ray diffraction patterns of (a) Nylon 6 crystalline structures α -form (at 20.5° and 24°) (b) Nylon 6 crystalline structures γ -form (at 21.5°), (c) nylon 6 nanocomposites with loading 2.5 wt.% Nanoclay, (d) nylon 6 nanocomposites with loading of 5 wt.% Nanoclay and (e) nylon 6 nanocomposites with loading of 10 wt% Nanoclay.

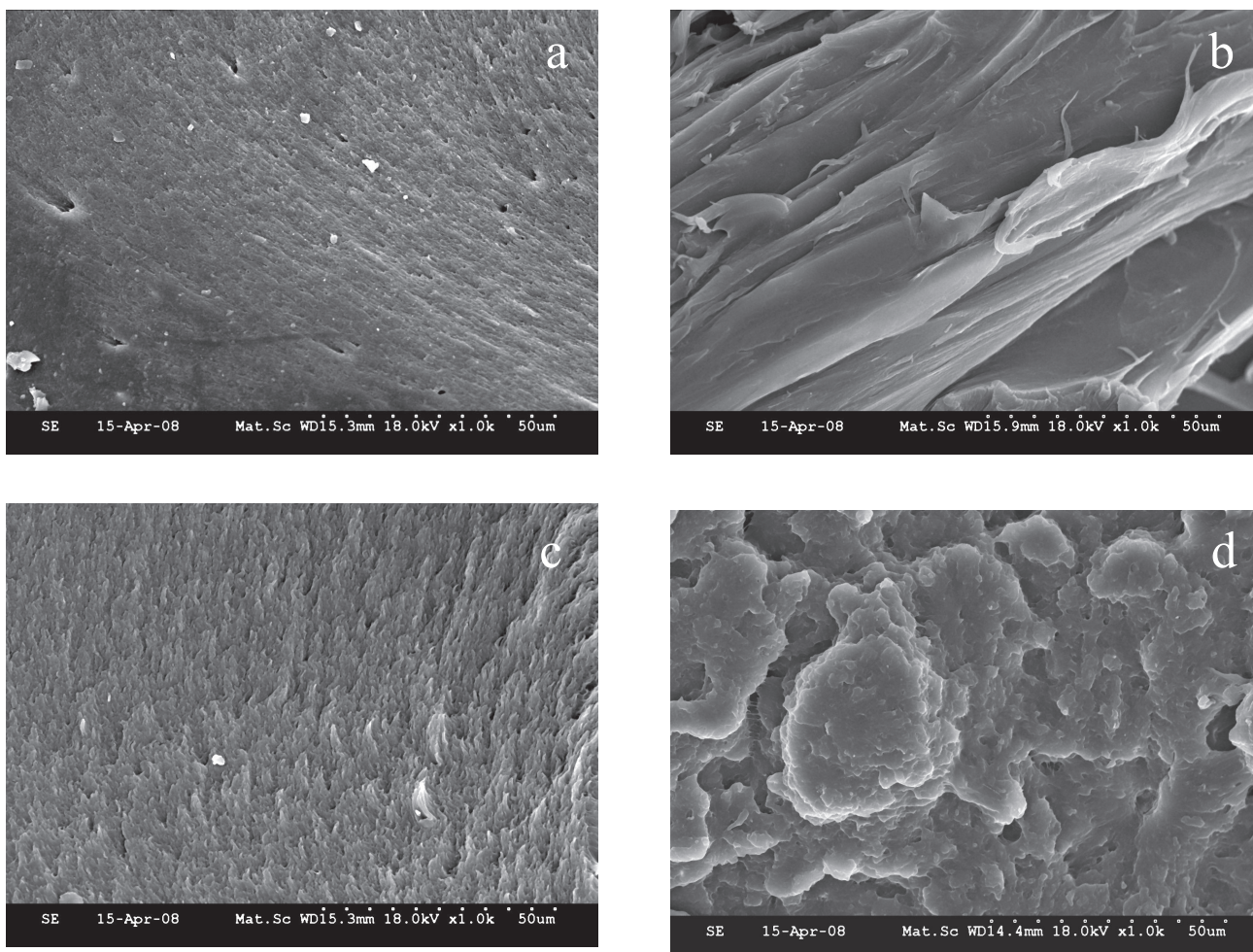


Fig. 4. SEM micrograph of fracture surface of (a) nylon 6, (b) nylon 6 containing 2.5 wt% of Nanoclay, (c) nylon 6 containing 5 wt% of Nanoclay and (d) nylon 6 containing 10 wt% of Nanoclay

properties than Nylon-6/fiber composites [11]. The mechanical properties of composites increase substantially relative to neat nylon 6 as the amount of organoclay is increased.

In the tensile test, it was found that tensile strength increases with increasing organoclay content by 10 wt. %. Izod impact test results showed enhancement of the stiffness and strength with increasing amount of clay in composites. This is due to the incorporation of clay platelets within the nylon 6 matrix.

Figure 4 (a, b, c and d) show the tensile fracture surface of the nylon 6 and its nanocomposites by loading of 2.5 wt%, 5 wt% and 10 wt% at magnification of x1.0 K respectively. SEM micrograph of nylon 6 showed mixed mode failure with extensive voiding. With 2.5 wt. % nanoclay dispersed in Nylon 6 nanocomposites showed rough fracture surface with large facets.

It indicated the formation of strong bonding

between nanoclay and nylon 6 and incorporation of ductility in the composite. With increase in the clay loading up to 5 wt%, the facets (fibrils) were observed to appear much finer and fractured surfaces were found to be less rugged while in case of further loading of Nanoclay i.e. 10 wt. %, matrix deformation was greatly reduced. The fracture surface was found to be featureless and no fibril sites were observed. This indicates that with loading higher than 2.5 wt. %, polymer becomes brittle.

Conclusions

Composites were fabricated with nylon 6 as matrix. The DSC results of nylon 6/nanoclay nanocomposites indicate the increasing in the crystallization temperature by 17.230C but the degree of crystalline decreased by 0.74% due to barrier effect on higher nanoclay contents, 10 wt.

% . The results of Heat Distortion Temperature (HDT) analysis showed enhancement of HDT at 264 psi from 60 to 85.9 with 10 wt. % loading of nanoclay. X-ray diffraction analysis of nylon 6/nanoclay nanocomposites indicates that the nylon 6 nanocomposites have γ -phase crystalline structure (peak at 21.5°). Also, the basal spacing of organoclay also increased up to 34.88 \AA . The mechanical properties of composites increase substantially relative to neat nylon 6 as the amount of organoclay is increased.

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