## Studies on Nylon 6/Clay Nanocomposites by Melt-Intercalation Process

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**ABSTRACT:** The preparation of nylon 6/clay nanocomposites by a melt-intercalation process is proposed. X-ray diffraction and DSC results show that the crystal structure and crystallization behaviors of the nanocomposites are different from those of nylon 6. Mechanical and thermal testing shows that the properties of the nanocomposites are superior to nylon 6 in terms of the heat-distortion temperature, strength, and modulus without sacrificing their impact strength. This is due to the nanoscale effects and the strong interaction between the nylon 6 matrix and the clay interface, as revealed by X-ray diffraction, transmission electron microscopy, and Molau testing. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1133–1138, 1999

Key Words: nylon 6; nylon 6/clay nanocomposite; melt intercalation; hybrid

#### INTRODUCTION

Polymer composites have been widely used in areas of electronics, transportation, construction, and consumer products. They offer unusual combinations of stiffness and toughness that are difficult to attain from individual components. Nanocomposites are defined by the particle size of the dispersed phase having at least one dimension less than  $10^2$  nm.<sup>1</sup> Because of the nanoscale features, nanocomposites possess superior physical and mechanical behaviors over their more conventional microcomposite counterparts and therefore offer new technology and business opportunities.

One promising strategy for synthesizing nanocomposites is the intercalation of monomers or polymers into layered silicate hosts. In most cases, the synthesis involves either intercalation of a suitable monomer and then exfoliating the layered host into their nanoscale elements by subsequent polymerization or polymer intercalation from a solution. But, for most technologically important polymers, both approaches are limited since neither a suitable monomer nor a compatible solvent system is always available.

Polymer melt-direct intercalation is a promising new approach to fabricate polymer-layered silicate nanocomposites by using a conventional polymer extrusion process. The formation of nanocomposites via melt intercalation depends upon the thermodynamic interaction between the polymer chains and the host silicates and the transport of the polymer chains from the bulk melt into the silicate layers. Previous studies $^{2-4}$ at Cornell University showed that by prudent choice of the interlayer cation the unfavorable loss of the conformational entropy associated with the intercalation of less interacting nonpolar polystyrene chains into silicate interlayers can be overcome and the mass transport of polymer chains into the layered silicate appears to be unhindered by the confinement of the chains. However, it is still unclear if this picture would hold true for more strongly interacting polar polymers.

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**Figure 1** A conceptual picture of nanocomposites obtained through melt intercalation. The rectangular bars represent the silicate layers. (a) Single polymer layers intercalated in the silicate galleries; (b) composites obtained by exfoliation of the silicate particles and dispersion in a continuous polymer matrix.

In this report, we discuss the melt-intercalation nanocomposites having polar nylon 6 as the matrix and organoclay as the dispersed phase. The properties of the nylon 6/clay nanocomposite were superior to the nylon 6 matrix in terms of the heat-distortion temperature, strength, and modulus without sacrificing its impact strength. Crystallization behaviors of the nanocomposite were studied by DSC. The nanostructure features were revealed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The aim of this work was to clarify the possibility of synthesizing nylon 6/clay nanocomposites via a melt-intercalation process. A conceptual illustration of melt-direction intercalation is shown in Figure 1.<sup>1</sup>

#### EXPERIMENTAL

#### **Materials**

Sodium montmorrillonite was kindly provided by the Institute of Chemical Engineering and Metallurgy, Chinese Academy of Sciences, with a particle size of 40–75  $\mu$ m, cation-exchange capacity (CEC) of 100 meq/100 g, and interlayer spacing of 0.98 nm. Organically modified montmorrillonite (organoclay) was synthesized, as previously outlined,<sup>5</sup> by a cation-exchange reaction between sodium montmorrillonite and octadecylammonium salt. The presence of octadecylammonium cations in the galleries provides hydrophobicity to the sodium montmorrillonite.

The nylon 6 used in the present work was produced by the Yangzhou Organic Chemical Engineering Corp., with a relative viscosity of 2.5. Before using, nylon 6 was air-dried at 80°C for 12 h, then dried under a vacuum at 80°C for 6 h to eliminate the water absorbed during the industrial washing.

#### **Sample Preparation**

Nylon 6/clay nanocomposites were synthesized using the following procedure: Organoclay and nylon 6 were mechanically mixed and then extruded by a twin-screw extruder at a rotational speed of 30 rpm. The temperature profiles of the barrel were 180–210–230–220°C from the hopper to the die. This extrudate was pelletized, dried, and injected into standard samples for mechanical testing. The injection-molding temperature and pressure were 220°C and 13.5 MPa, respectively.

#### **Measurement and Characterization**

XRD was performed at room temperature by a Rigaku Model D/max-2B diffractionmeter; the X-ray beam was nickel-filtered CuK $\alpha_1$  ( $\lambda = 0.154$  nm) radiation operated at 40 kV and 30 mA; data were obtained from 1° to 40° (2 $\theta$ ) at a rate of 1°C/min. The dispersion of the clays in the nylon



**Figure 2** XRD scans for (a) organoclay and (b) nylon 6/clay nanocomposites (10.5 wt %).



**Figure 3** High-resolution transmission electron micrograph of nylon 6/clay nanocomposites.

6 matrix and the nanofeatures were observed through microscopic investigations on an H-800 transmission electron microscope at 100 kV. The Molau testing<sup>6-8</sup> was to study the interaction between the nylon 6 matrix and the organoclay. In a typical example, first we put 0.8 g of the nanocomposites and nylon 6 samples into a test tube, then added 8-mL formic acid to obtain the formic acid solutions for stability contrasting. Differential scanning chromatography (DSC) was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating or cooling rate of 5°C/min under a nitrogen atmosphere; the temperature range was from 80 to 250°C. The mechanical properties were examined with an Instron universal testing machine Model 1122 at a crosshead speed of 2 mm/min and at room temperature.

### **RESULTS AND DISCUSSION**

#### **Microstructure of Nanocomposites**

The change of the interlayer distance can be detected by XRD. Figure 2 shows the XRD patterns of both the organoclay and the nylon 6/clay hybrid. The XRD pattern of the organoclay shows a characteristic peak ( $d_{001} = 1.55$  nm) at 5.7° of 2 $\theta$ . After melt intercalation, the intensity of the diffraction peak corresponding to the organoclay is considerably reduced while a new peak ( $d_{001} = 3.68$  nm) appears at 2.48° of 2 $\theta$  corresponding to the unexfoliated nylon 6/clay hybrid. On the other hand, the characteristic diffraction peak of the nylon 6/clay hybrid (2.48° of 2 $\theta$ ) was not detected when the clay content of the

nanocomposites was lower than 10 wt %. These results imply that the intercalated silicate layers through the melt-extrusion process are exfoliated into nanoscale layers and randomly dispersed in the nylon 6 matrix. This interpretation can be evidenced by TEM of Figure 3.

Figure 3 shows a high-resolution TEM image of nylon 6/clay hybrids. The white light area is the nylon 6 matrix and the black area is made up of the silicate layers. It can be seen that the silicate layers disperse evenly in the matrix. The microstructure of the hybrids is similar to that of organoclay, but the interlayer distance is expanded to 3–5 nm, which is compatible with the XRD result. In addition, from the statistics computation, the particle size of the layered silicates in the nylon 6 matrix is reduced from the original  $40-70 \ \mu m$  to  $20-50 \ nm$  through the melt-intercalation process. All those results demonstrated that most of the silicate layers are exfoliated into nanometer layers and randomly dispersed in the nylon 6 matrix via a melt-intercalation process.

The Molau testing result, illustrated in Figure 4, shows the strong interaction between the nylon 6 matrix and the organoclay nanoparticles. The organoclay in the composites is well distributed in



**Figure 4** Molau testing showing the dispersion state of samples in the formic acid solutions: (a) nylon 6/clay microcomposites; (b) nylon 6/clay nanocomposites.



**Figure 5** XRD scans for (a) nylon 6 and (b) nylon 6/clay nanocomposites.

the formic acid and does not subside; however, the conventional counterpart of the nylon 6/clay microcomposite subsides in the formic acid, which is compatible with the TEM results.

# Crystal Structure and Crystallization Behavior of Nanocomposites

Nylon 6 is a type of multicrystalline-form polymer.<sup>8</sup> It often has the more stable  $\alpha$  form rather than the  $\gamma$  form. The XRD study shows that the addition of clay has the effect of promoting the formation of the  $\gamma$  form.

Figure 5 shows XRD patterns of the nanocomposite and the nylon 6 matrix. Both the polymer matrix and nanocomposites exhibit two  $\alpha$  crystalline diffraction peaks. However, besides these two peaks, the nanocomposites exhibit an additional distinct  $\gamma$  crystalline diffraction peak at 21.5° of



**Figure 6** DSC heating scans of samples (a) nylon 6 and (b) nylon 6/clay nanocomposites.



**Figure 7** DSC cooling scans of samples: (a) nylon 6; (b) nylon 6/clay, 10 wt %; (c) nylon 6/clay, 5 wt %; (d) nylon 6/clay, 3 wt %; (e) nylon 6/clay, 1 wt %.

 $2\theta$ . The clay-induced  $\gamma$  crystalline form is also shown by the DSC heating scans. From Figure 6, it can be seen that the nylon 6 matrix has only one melting peak corresponding to the  $\alpha$  crystalline form, but the nanocomposite system has two melting peaks, in which the high-temperature peak corresponds to the  $\alpha$  form and the low-temperature peak corresponds to the  $\gamma$  crystalline form.

The effect of the clay content on the crystallization behavior of nylon 6 was studied by DSC cooling scans. Figure 7 shows the DSC results. Both the composites and the nylon 6 have only one exothermic peak, but the peak forms and peak temperatures of the nanocomposites differ from those of the polymer matrix. The presence of



**Figure 8** Effect of clay content (wt %) on nylon 6/clay nanocomposites' relative crystallinity and supercooling extent.



**Figure 9** Heat-distortion temperature of nylon 6/clay nanocomposites.

clay in the nanocomposites increases the crystallization temperature of nylon 6 and narrows the width of the crystalline peak. It can be concluded that the clay increases the crystallization rate and has a strong heterophase nucleation effect on nylon 6. The effects of the clay on the relative crystallinity and the supercooling extent of the nylon 6 matrix are shown in Figure 8. The relative supercooling extent is considerably reduced from 0.22 to 0.15, corresponding to the clay content from 0 to 1.4 wt %, but changes less when the clay content continues to increase. On the other hand, the clay content has less effect on the relative crystallinity. The relative crystallinity is basically constant when the clay content changes from 0 to 6.7 wt %.

#### **Mechanical Testing**

The effects of the clay content on thermal and mechanical properties of the nylon 6/clay nano-



**Figure 10** Flexible properties of nylon 6/clay nanocomposites.



**Figure 11** Effect of clay content on tensile modulus of nylon 6 clay nanocomposites.

composites are summarized in Figures 9-12. The heat-distortion temperature increases rapidly with an increasing clay content from 0 to 5 wt %, but the change is less when the clay content increases beyond 5 wt %. Similarly, the flexual modulus increases rapidly with increasing clay content from 0 to about 3.5 wt %, but increases little for a clay content higher than 3.5 wt %. The flexural strength approaches the highest point at about 3 wt % and decreases with further increment of the clay content. The tensile modulus increases rapidly with the clay content in the range of 0-15 wt %, but changes little for a clay content higher than 15 wt %. On the other hand, the notched impact strength is basically constant within the experimental error in the clay content range of 0-17%.



Figure 12 Effect of clay content on notched Izod impact strength of nylon 6/clay nanocomposites

Properties	Nylon 6/Clay Nanocomposites	Nylon 6
Yield strength (MPa)	91.3	68.2
Tensile modulus (GPa)	4.1	3.0
Flexural strength (MPa)	150	93.5
Flexural modulus (GPa)	4.2	2.4
Notched Izod impact strength (J/m)	26.0	28.0
Heat distortion temperature (°C) 1.82 MPa	112	62

Table IProperties of Nylon 6/Clay Nanocomposites (4.2 wt %)

As one example, Table I illustrates the properties of the nanocomposites with a 4.2% clay weight content. It can be seen that the heat-distortion temperature increased from  $62^{\circ}$ C for the nylon 6 matrix to  $112^{\circ}$ C. Similarly, the yield strength, flexural strength, and modulus all have been much improved. At the same time, the notched impact strength is not sacrificed. The performance improvements of the nanocomposite at a low filler content was far superior to those of conventional counterpart composites.

From the above results, it can be summarized here that the nanocomposites prepared by melt intercalation can attain superior performance over their conventional counterparts. This highreinforcement effect implies a strong interaction between the matrix and the clay interface that can be attributed to the nanoscale and uniform dispersion of the silicate layers in the nylon 6 matrix. The project was supported by the National Nature Science Foundation.

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