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Phase transition in nylon 6/clay nanocomposites on annealing

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Abstract

The $\gamma \rightarrow \alpha$ crystalline phase transition in nylon 6/clay nanocomposite prior to melting was investigated by X-ray diffraction. The phase transition in the nanocomposite took place at 160 °C, 40 °C higher than that of nylon 6 at 120 °C. The transition extent in the nanocomposite was lower than that in nylon 6. This could be caused by the strongly confined spaces between layers, and the favorable environment for the formation of the γ phase in the existence of clay. Besides, the less grown crystallites of the α phase transformed from the γ phase in the nanocomposite began to melt at much lower temperature than its normal melting temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6/clay nanocomposite; Phase transition; X-ray diffraction

1. Introduction

Many semicrystalline polymers undergo crystalline phase transitions prior to melting. The crystal-to-crystal phase transition in nylon 66 was observed first in polyamide and known as Brill transition, which has been studied extensively [1–6]. Upon heating nylon 66, the room temperature triclinic structure transforms into a different triclinic structure, the Brill transition in nylon 66 is clearly displayed in X-ray diffraction study, as two prime strong reflections at ~20° (200) and ~24° (002 + 202) merge into a single reflection at the transition temperature [1]. The crystal-to-crystal phase transition prior to melting in nylon 6 was also observed and studied by some researchers using FT-IR, NMR and XRD [4,5,7,8].

In recent years, polymer/clay nanocomposites have attracted great interest from researchers. The reason is that they frequently exhibit unexpected hybrid properties synergistically derived from two components. The unprecedented improving in performance of the nanocomposites was first demonstrated by a group at the Toyota research center in Japan using nylon 6/clay nanocomposites [9–11]. Since then, many polymer/clay nanocomposite systems have been investigated and prepared. Though the improved properties were achieved, the nature, origin and some unique behaviors of such nanocomposites are not well understood. For example, as the first and most successful polymer/clay nanocomposites, there are few articles dealing with crystallization behavior and crystal structure of nylon 6/clay nanocomposite [12–16].

In previous study, we prepared a nylon 6/clay nanocomposite (N6CN) via melt compounding using a novel kind of co-intercalation organophilic montmorillonite clay obtained by co-intercalation of epoxy resin and quaternary ammonium into Na-montmorillonite. The highly improved properties will be published elsewhere. In this study, we would like to report its phase transition behavior prior to melting under annealing condition.

2. Experimental section

Nylon 6, Ultramid B3 used in this study was manufactured by BASF. The cation exchange capacity (CEC) of Na-montmorillonite used in this article was 80 meq/100 g. The particle size was less then 20 μm. Epoxy resin ARALDITE GY 240, the diglycidyl ether of bisphenol A with a molecular weight of 360, was purchased from Ciba–Geigy.

The co-intercalation organophilic clay used in this study was prepared as follows in two steps: (1) 100 g Na-montmorillonite was dispersed into 5000 ml of hot water using homogenizer. 30 g hexadecyl trimethyl ammonium bromide was dissolved into hot water and poured into the Na-montmorillonite–water solution under vigorous stirring for 30 min to yield white precipitates. The precipitates were collected and washed by hot water three times, and then the

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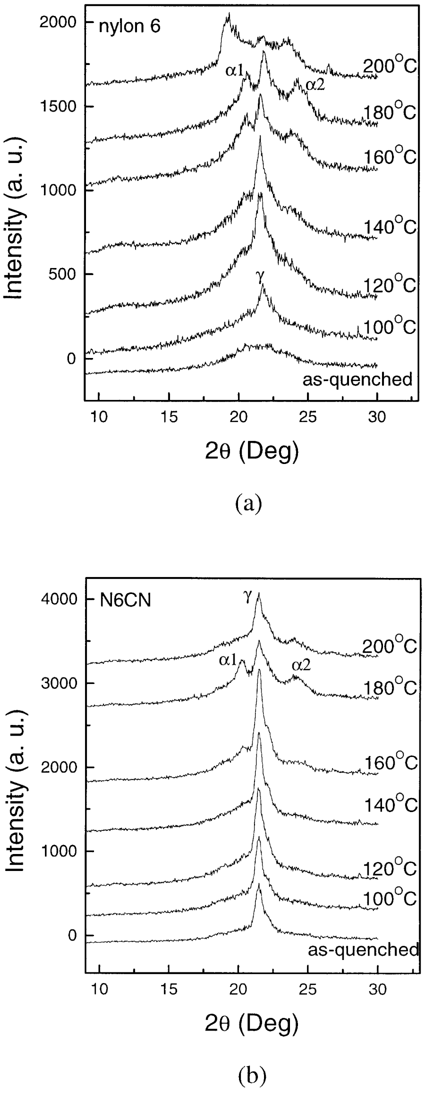


(a)

(b)

Fig. 1. XRD patterns of nylon 6 and N6CN annealed at different temperatures.

precipitates were ground into the size of 20 μm after thorough drying in a vacuum oven. The obtained precipitates and the like was a kind of organophilic clay widely used in polymer/clay nanocomposites; (2) 130 g precipitates obtained in step 1 and 20 g epoxy resin GY 240 were mixed in a Haake Reocorder 40 mixer for 1 h. Then the co-intercalation organophilic clay can be obtained.

A twin-screw extruder was used for the preparation of N6CN. Nylon 6 granules were dried in a vacuum oven at 120 °C for 24 h prior to blending with co-intercalation organophilic clay. The temperature of the extruder was maintained at 220, 245, 245 and 230 °C from hopper to die, respectively. The screw speed was maintained at 180 rpm. The obtained nanocomposite containing 5 wt% clay was used in this study.

In order to eliminate the influence of specimen thickness, ca. 100 μm films of nylon 6 and N6CN were prepared for annealing: The granules were put between two glass slides, then heated in oil-bath up to 250 °C. After the granules had entirely molten, they were kept at this temperature for 10 min to eliminate the heat history, a load was applied on the surfaces of slides to press the molten materials into thin films, and then the thin films were quickly removed from oil-bath and quenched in liquid nitrogen.

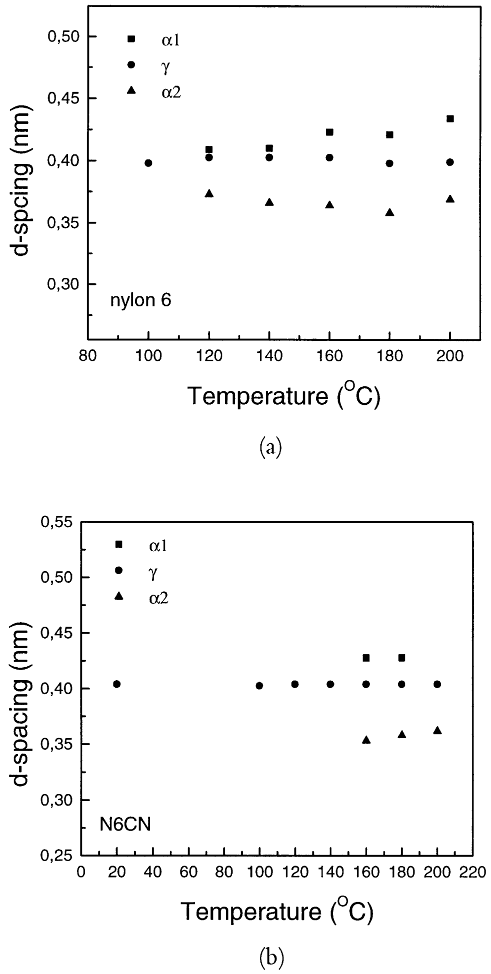
Afterwards, the quenched films were annealed in oil-bath at different temperatures for 1 h, then the films were removed and quenched in liquid nitrogen again to be tested by XRD.

X-ray diffraction patterns of the annealed films were recorded by a Siemens D5000 X-ray diffractometer at room temperature. The Cu K_α radiation source was operated at 40 KV and 20 mA. Patterns were recorded by monitoring those diffractions that appeared from 1.5 to 30°. The scan speed was 2°/min. A Perkin Elmer DSC-7 differential scanning calorimeter was used to evaluate the thermal property of nylon 6 and N6CN. About 10 mg sample cut from the quenched film was heated from 30 to 250 °C at a rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

The nylon 6 sample quenched in liquid nitrogen is amorphous as evidenced by XRD in Fig. 1(a). When the quenched film is annealed at 100 °C for 1 h, a sharp diffraction peak appears at $2\theta = 21.8°$ contributed by the γ crystalline phase of nylon 6. Two additional diffraction peaks, more exactly shoulders, appear in the XRD pattern of the nylon 6 after being annealed at 120 °C for 1 h. The two peaks, one at $2\theta = 20.3°$ (α1) and another at $2\theta = 23.7°$ (α2), are the distinctive feature of the α crystalline phase of nylon 6. After being annealed at 140 °C, the diffraction peaks of the α phase become larger while the γ phase is still dominant. When the annealing temperature is increased up to 160 °C, the diffraction peaks of the α phase continue growing but the peak of the γ phase begins to decrease. Higher annealing temperature amplifies this trend, upon annealing at 200 °C for 1 h, the most prominent peak is caused by the α phase. Besides, during the growth of the α phase with increasing annealing temperature, α1 peak shifts to lower angle and α2 peak shifts to higher angle.

In a sharp contrast to nylon 6, N6CN quenched in liquid nitrogen crystallizes into the γ phase as presented in Fig. 1(b). In addition to highly improved mechanical and thermal properties, we also observed some unique crystallization behaviors in N6CN by compounding with such a new co-intercalation organophilic clay: N6CN favored the formation of the γ crystalline phase; the crystallinity degree of N6CN showed strong dependence on cooling rates, the higher the cooling rate, the higher crystallinity degree could be observed. The extreme example is that N6CN maintains highly ordered structure even quenched in liquid nitrogen as presented in Fig. 1(b), which needs further study and will be published elsewhere. When the sample is annealed at 100 °C



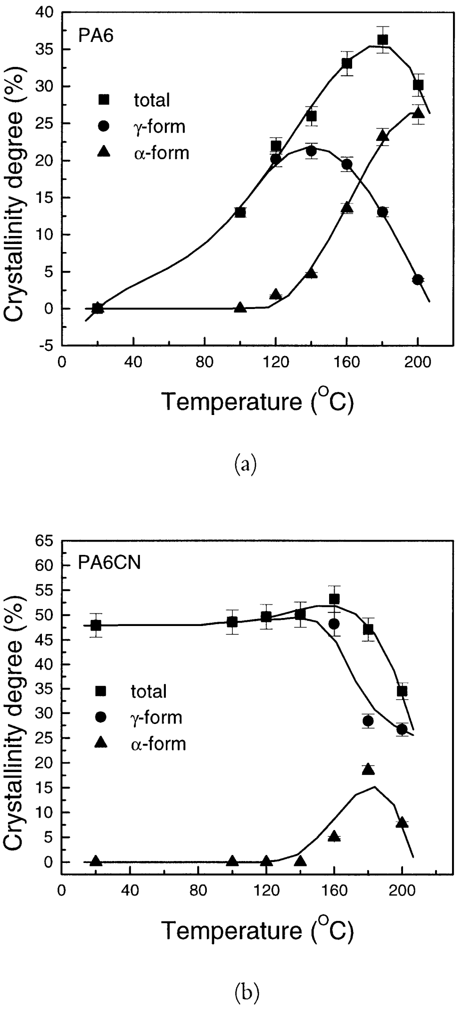
(a)

(b)

Fig. 2. Plots of the *d*-spacings as a function of temperature in nylon 6 and N6CN.

for 1 h, N6CN still maintains the characteristic diffraction peak of the γ phase at 21.8°. Two diffraction peaks corresponding to the α phase appear at 160 °C. The peaks of the α phase reach their maximum when annealed at 180 °C, while the peak of the γ phase begins to decrease. However, the peaks of the α phase begin to decrease at higher temperature, α1 peak even disappears when sample is annealed at 200 °C. Though the peak intensity decreases with increasing annealing temperature, the γ phase is still dominant in the XRD pattern.

The changes in the *d*-spacing of the nylon 6 annealed at various temperatures are plotted in Fig. 2(a). In the whole temperature range, the *d*-spacing corresponding to the γ phase maintains its value without large variation. The *d*-spacings due to the α1 and α2 peaks at 0.41 and 0.37 nm appear from 120 °C. With increasing annealing temperature, the *d*-spacing due to the α1 increases up to 0.43 nm at 200 °C, while the *d*-spacing of the α2 decreases to 0.359 nm at 180 °C. The nature of the phase transition prior to melting is considered to the effect of conformational motion due to temperature variation and is associated with a packing change within the crystal [1]. Thus at certain temperature, 120 °C in this case, the α phase begins to replace the γ phase as shown in Figs. 1(a) and 2(a). The α1 peak arises from the distance between hydrogen-bonded chains, and the α2 peak arises from the separation of the hydrogen-bonded sheets [4,17]. The increase in the *d*-spacing of the α1 at higher temperature could be due to the thermal expansion of the lattice, while the decrease in the *d*-spacing of the α2 is caused by respective lattice distortion. The extent of the phase transition in the nylon 6 can be analyzed from Fig. 3(a). The crystallinity degree of the α phase increases greatly from 0 up to 26.4% at 200 °C that contributes most of the total crystallinity degree at this temperature. The highest crystallinity degree of the γ phase is observed when the sample is annealed at 140 °C. The total crystallinity degree increases sharply up to 35.1% at 180 °C. From above results, the phase transition of nylon 6 begins from 120 °C and lasts up to 200 °C; the transition extent increases with increasing annealing temperature.



(a)

(b)

Fig. 3. Plots of the crystallinity degrees as a function of temperature in nylon 6 and N6CN.

The changes in the *d*-spacing of N6CN during annealing

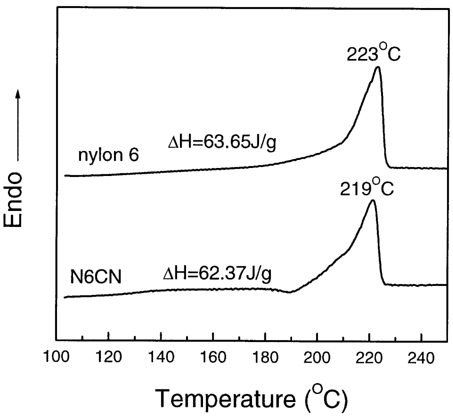


Fig. 4. DSC heating scan thermograms of nylon 6 and N6CN.

process are presented in Fig. 2(b). Similar to nylon 6, the *d*-spacing due to the γ phase maintains its value in whole temperature range. The *d*-spacings due to the $\alpha 1$ and $\alpha 2$ peaks at 0.426 and 0.353 nm appear at 160 °C. When annealed at 200 °C, the *d*-spacing of the $\alpha 1$ disappears. The extent of the phase transition in N6CN is presented in Fig. 3(b). The crystallinity degree of the γ phase increases slightly before 160 °C, then it decreases sharply; while the crystallinity degree of the α phase increases fairly after 160 °C. The sharp decrease in crystallinity degree of the α phase at 200 °C will be explained later. The results of Figs. 1(b), 2(b) and 3(b) indicates that the onset of phase transition in N6CN takes place at 160 °C, 40 °C higher than that of nylon 6; the transition extent in N6CN is lower than that in nylon 6.

The higher phase transition temperature and lower transition extent in N6CN could be caused by the strongly confined polymer molecular chains between silicate layers. As mentioned previously and presented in Fig. 1(b), N6CN favors the formation of the γ crystalline phase even quenched in liquid nitrogen. Vaia et al. [18]suggested that the proximity of the surface of layers results in conformation changes of chains, limiting the formation of hydrogen bonded sheets leading to the appearance of the γ phase; and the strongly confined space formed by the layers restricts the mobility of nylon molecular chains. Though α phase is more stable than γ phase, the transition still need more energy at higher temperature to overcome the restriction, and only the part less influenced by silicate layers can undergo phase transition effectively.

Fig. 4 presented the DSC heating scan of nylon 6 and N6CN. Nylon 6 has a 223 °C peak melting temperature (T_m) while the melting process begins from about 210 °C. The T_m peak of N6CN is 219 °C and the melting begins from ca. 190 °C. That is to say, the disappearance of the $\alpha 1$ peak of N6CN at 200 °C is caused by the melting at lower temperature. As noted by Campoy [19], T_m associated to the α phase is 223 °C and γ phase of nylon 6 is 219 °C. The DSC result clearly indicates that the α phase is dominant in nylon 6 prior to melting after heating. However in the case of N6CN, though peak T_m of the α phase is higher than that of the γ phase, the less grown, smaller crystallites of the α phase transformed from γ phase, which caused by the restriction of the strongly confined spaces and the favorable environment for the γ phase by silicate layers, begin to melt at much lower temperature. The γ phase becomes dominant prior to melting.

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