Characterization of nylon 6/11/montmorillonite nanocomposites prepared by in situ copolymerization

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Abstract: A novel nylon 6/11/montmorillonite nanocomposite was prepared by in situ copolymerization of prepolymer of caprolactam with aminoundecanoic acid in the presence of organoclay, and characterized in terms of Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), transmission electron micrograph (TEM), intrinsic viscosity as well as differential scanning calorimetry (DSC). It was found that the addition of organoclay had great influence on the intrinsic viscosity and melting behavior but not on the crystal transition of nylon 6/11 matrix. Intercalated/exfoliated and stacked silicates layers were observed for various nanocomposites.

Keywords: Nylon 6/11; nanocomposite; characterization.

Introduction

Nylon 11 has potential application on the manufacture of Micro-Electro-Mechanical Systems (MEMS) sensors due to its curious piezoelectric and ferroelectric responses [1]. Additionally as one of the engineering plastics with high performance, nylon 11 has been developed for various applications ranging from automotive to offshore oilfield. Especially, nylon 11 is a promising engineering plastic since its starting material originates from a regenerative castor plant. The wider application, however, is severely restricted by its relatively high yield cost. Many works have been carried out to solve this limitation [2]. In our laboratory, we synthesized successfully nylon 6/11 by hydrolytic polymerization and melt polycondensation [2c].

Polymer/layered silicate nanocomposites (PLSNs) have attracted much attention in the last decade due to their increased modulus and strength and improved thermal and barrier properties. The pioneering work on nylon 6/clay hybrid nanocomposite was first developed by Toyota research group [3]. Encouraged by the successful commercialization of nylon 6/clay nanocomposite, nylon 11-, nylon 1012-, nylon 1010, nylon 12-based clay nanocomposites were prepared successively and displayed excellent thermal and mechanical performances [4]. To date no literature on nylon 6/11/clay nanocomposite has been published to the best of our knowledge. In the present study, a series of nylon 6/11 based clay nanocomposites with different organoclay content has been synthesized by in situ copolymerization and characterized in terms of chemical and crystal structure, melting and crystallization behavior.

Results and discussion

FTIR

The spectrum of pristine clay displays two characteristic peaks at 1037cm^{-1} and 561cm^{-1} (Fig.1 curve a). After modification of pristine clay with aminoundecanoic acid, the spectrum of organoclay (Fig.1 curve b) exhibits three new peaks. The two peaks at 2933cm^{-1} and 2856cm^{-1} have been assigned to CH stretching in the aminoundecanoic acid units, and the other peak at 3300cm^{-1} results from the N-H stretching. Such phenomena demonstrate that aminoundecanoic acid successfully diffuses into the clay galleries. In the spectra of nylon 6/11 (Fig.1 curve c) and its nanocomposites (Fig.1 curve d), some typical polyamide peaks are observed at 3304cm^{-1} (N-H stretching), 1643cm^{-1} (C=O stretching, amide), 1545cm^{-1} (N-H bending, amide II), 721cm^{-1} (amide V), and 563cm^{-1} (amide VI). As comparison with the spectrum of nylon 6/11, three new peaks, although very weak but distinguishable, are observed in the spectra of nanocomposites at 1037cm^{-1} , 563cm^{-1} , and 466cm^{-1} , which are characteristic peaks of organoclay.

Fig. 1. FTIR spectra of (a) Pristine clay, (b) Organoclay, (c) Nylon6/11, and (d) Nanocomposite.

WAXD

The WAXD pattern (Fig. 2 curve a) of origin clay displays a reflection peak at $2\theta=6.27^\circ$, corresponding to a basal spacing of 1.41nm. For organoclay (Fig. 2 curve b), the reflection peak of the basal plane shifts to $2\theta=4.0^\circ$ with a d spacing of 2.21 nm. Such change demonstrates that aminoundecanoic acid diffuses into the clay galleries and thus increase the layer distance. It is worthy to notice that there is no peak of the (001) crystal plane to be observed in the WAXD pattern for the NC-3 (Fig. 2 curve d), which indicates that the organoclays are thoroughly exfoliated and disperse homogenously in the nylon 6/11 matrix. For NC-5 and NC-8 nanocomposites, however, a weak and broad peak appears, indicating that the silicate layer aggregates and/or reorders again in the case of high clay content.

Nylon 11 is known to exist in at least five crystal forms (α , β , δ , γ and δ'), which depend on the thermal history and testing temperature [5]. The WAXD patterns of both nylon 6/11 and its nanocomposites exhibit two strong reflections (100) and (010) at the diffraction angle 2θ of 20.2° and 23.4° , which are characteristic of the triclinic α form. It is indicated that the incorporation of organoclay has no influence on the crystal form of nylon 6/11.

Fig. 2. WAXD patterns of (a) Pristine clay, (b) organoclay, (c) nylon 6/11, (d) NC-1, (e) NC-3, (f) NC-8 and (g) NC-8.

TEM

WAXD provides a convenient way to determine the degree of clay intercalation by monitoring the position, shape, and intensity of the (001) diffraction peak from the dispersed nanoclays, while TEM allows direct visualization of the internal structure. The internal structure of the nanocomposites on the nanometer scale was directly observed by TEM analyses.

Fig. 3. Bright field transmission electron micrographs of (a) NC-3 and (b) NC-8.

Figure 3 illustrates the TEM bright-field images of NC-3 and NC-8 nanocomposites, in which dark entities are the cross section of intercalated organoclay layers and bright areas are the matrix. Intercalated and exfoliated organoclays (although few) disperse uniformly in the matrix in NC-3 (Figure 3a), while stacked silicates layers are evident in NC-8 (Figure 3b). According to the morphologies, we can explain well the WAXD patterns of the nanocomposites. Intercalation takes place when the polymer penetrates the silicate gallery, the intercalated distance (a few nanometers) is increased, which means a broad peak toward to a lower angle. If through exfoliation (total separation of the silicate nanoplatelets by polymer chains) occurs, the peak of the (001) crystal plane disappears.

Intrinsic viscosity

As can be seen in Figure 4, the intrinsic viscosities ($[\eta]$) of the resulting nanocomposites decrease to a little degree as the initiate addition of organoclay. However, the value of $[\eta]$ reduces sharply in the case of 3 wt% of organoclay and then levels off as the organoclay loading increases. The copolymerization rate is believed to slow down due to the constrained chain mobility of the monomers in the vicinity of the organoclay. Additionally, it is speculated that the organoclay blockades the active ending-group of the monomers and thus reduces the amount of the available activator sites.

Fig. 4. Variation of intrinsic viscosity with organoclay content.

DSC thermal analysis

The melting and crystallization behaviors of nylon 6/11 and its nanocomposites were examined using DSC, and their corresponding thermograms are presented in Figure 5. A melting peak at 209.5 °C (Fig.5 a) and a crystallization peak at 173.8 °C (Fig.5 b) are observed for nylon 6/11 in the DSC heating and cooling thermograms, respectively. It is inferred that a homopolymer of nylon 6 is formed during the synthesis of nylon 6/11. We reported in other publication [2c] that only random copolymer is formed in the case of copolymerization of aminoundecanoic acid with caprolactam. Furthermore, other double melting peaks at I and II are observed for all specimens. The melting peak I at low temperature shifts towards the lower

temperature and becomes more intensive, the melting peak II at high temperature becomes weaker with the increasing organoclay content (except NC-1). The double melting endotherms can be attributed to two different crystal structures, different crystal size and perfection, re-crystallization or different thermal history [6]. Since only triclinic α form of crystal structure was demonstrated by WAXD, the melting peak at low temperature is assumed to be due to the melting of crystals formed on cooling from melt, while the second peak is mainly due to melting of crystals which have re-crystallized during the heating run (after the first melting peak). Additionally, it is observed nucleating action of the organoclay only on thermograms of NC-1 composition, its crystallization temperature is also higher than that of other nanocomposites. Organoclay probably really facilitate the formation of one crystal form.

Fig. 5. DSC heating (a) and cooling thermograms (b) of nylon 6/11 and its nanocomposites with various organoclay contents.

Conclusions

Nylon 6/11-based nanocomposites with various organoclay contents were prepared by combination of hydrolytic polymerization and melt polycondensation. The organoclays were thoroughly exfoliated and dispersed homogenously in the nylon 6/11 matrix in the case of low organoclay loading ($\leq 3\%$). Although the organoclay content influenced the melting and crystallization behavior of nylon 6/11 matrix, it could not transmit the crystal forms of the copolymer matrix.

Experimental part

Materials

The aminoundecanoic acid was supplied by Taiyuan Zhonglian Zenong Chemical Industry Co. (China, Taiyuan), and was re-crystallized using deionized water prior to use. The caprolactam was purchased from Yueyang Petrochemical Co. (China, Yueyang), and was dried-vacuum under 80 °C for 12 h. Sodium montmorillonite was provided by Zhejiang Hongyu Clay Chemical Co., Ltd (China, Anji).

Treatment of montmorillonite

In the present article, the organoclay was prepared as follows: 100 g original clays were dispersed into 5000 ml hot deionized water using a homogenizer. Aminoundecanoic acid (8.0g) and concentrated hydrochloric acid (4 ml) were dissolved in hot water (200 ml) and then poured into the clay water suspension under vigorous stirring for 12 h. The product was filtered off and washed with deionized water several times. The final product (donated as organoclay) was dried in a vacuum oven at room temperature for 48 h and grounded into powder.

Preparation of prepolymer of caprolactam

To an autoclave equipped with mechanical stirrer, a gas inlet and a gas outlet was added the weighed caprolactam and deionized water. After the oxygen was removed by repeat rinsing under pressure with purified nitrogen, the mixtures was heated to 190 °C and stirred for 2 h in autogenous pressure additions. The reactor was then decompressed to ambient pressure mean while heated to 230 °C, and the polymerization was kept under vacuum and stirring conditions for 0.5-1 h at 230 °C. After completion of copolymerization, the molten prepolymer was drawn through the bottom valve, cooled and granulated. The prepolymer pellets were extracted in an excess of deionized water to remove unreacted caprolactam or its dimmers.

Preparation of nylon 6/11/organoclay

To the above-described autoclave was added the weighed aminoundecanoic acid, prepolymer of caprolactam, organoclay and deionized water. The preparation procedures of nylon 6/11/organoclay were similar with that of prepolymer of caprolactam. The difference lies in that the copolymerization was kept under vacuum and stirring conditions for 1-5 h at 230 °C. The nylon 6/11-based clay nanocomposites were coded as NC-X, where X is the weight percentage of the organoclay relative to the total weight of aminoundecanoic acid and prepolymer of caprolactam. For example, NC-1 represents 1 wt % organoclay of aminoundecanoic acid and prepolymer of caprolactam.

Characterization

-FTIR

The Fourier transform-infrared spectroscopy (FT-IR) spectrum was performed with a FTIR-8400s spectrometer (Japan, Shimadzu Co.) employing a KBr pellet method, in which the sample was ground to powder.

-WAXD

The WAXD measurement was obtained in a Rigaku D/Max-Ra diffractometer (Japan) with curved graphite crystal filtered. The corresponding wide-angle X-ray diffraction patterns were collected in transmission mode ($\lambda=0.1542$ nm) at room temperature operating under a tube current of 100mA and an acceleration voltage of 40kV. The scanning rate was 40/min. The thin nanocomposite sheet with thickness of 0.5 mm was used for WAXD analysis while the clay was analyzed in powder form.

-TEM

Microstructure of nanocomposites was observed by using TEM (H-700 Hitachi Co.) operated at an accelerating voltage of 100 kV. The ultra thin section (the edge of the sample sheet perpendicular to the compression mold) with a thickness of 100 nm was microtomed at 80 °C using a Reichert Ultra cut cryo-ultramicrotome without staining.

-DSC

Measurements of the melting and crystallization behaviors were performed on a Mettler DSC822e (Switzerland, Mettler Co.), and the temperature was calibrated with the indium standard. DSC experiments were performed under a nitrogen purge at a constant flow rate. Sample weights were between 2-3mg. All specimens were dried at 80 °C under vacuum for 12 h before measurement. The sample was heated to 250 °C at a heating rate of 20 °C /min and kept isothermal for 10 min to eliminate any previous thermal history, and then cooled to room temperature at -10 °C /min and kept isothermal for 5 min. The sample was subsequently heated to 250 °C at a heating rate of 10 °C /min. The first cooling scan and the second heating scan were recorded.

-Intrinsic Viscosity

The molecular masses of the copolymer are expressed by their intrinsic viscosities, which were determined from measurements made on Solutions of the copolymers ($c=0.4, 0.33, 0.2$ and 0.13 g/100ml in m-cresol) with Ubbelohde viscometer at 25 °C.

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