Preparation and Properties of PET/PA6 Copolymer/Montmorillonite Hybrid Nanocomposite

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ABSTRACT: From *in situ* polycondensation, a poly(ethylene terephthalate)/Polyamide 6 copolymer/montmorillonite nanocomposite was prepared, after the treatment of montmorillonite (MMT) with a water soluble polymer. The resulting nanocomposites were characterized by X-ray diffraction (XRD), differential scanning calorimeter (DSC), nuclear magnetic resonance (NMR), dynamic mechanical analysis (DMA), and transmission electron microscopy (TEM). The results of DSC, ^{1}H NMR, and DMA proved that the nanocomposite synthesized was PET/PA6 copolymer/MMT nanocomposite, not the PET/PA6 blend/MMT nanocomposite. The results of XRD and TEM proved that the dispersion of MMT was improved observably after the introduction of PA6 molecular chain into PET. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2512–2517, 2006

Key words: poly(ethylene terephthalate); organoclay; nanocomposites

INTRODUCTION

In recent years, polymer/layered silicate nanocomposites have been a research focus of scientists from all over the world because of its tremendously improved properties such as excellent mechanical properties, thermal stability, gas barrier, and fire retardence compared with those of conventional composites.[1–11] Three kinds of nanocomposites, intercalated, flocculated, or exfoliated, will form according to the dispersion state of clay layers in polymer matrix. Usually an exfoliated nanocomposite has better properties than an intercalated one because of its better structure uniformity.

Poly(ethylene terephalate) (PET) is a widely used semicrystalline thermoplastic polyester with excellent properties such as very good barrier, crease resistance, solvent resistance, high melting point, resistance to fatigue, and high tenacity as either a film or a fiber. However, there is a continuing practical need to improve the performance properties of PET. Recently, in light of success in research of some polymer/clay nanocomposites, preparation of PET/clay nanocomposite has become another popular method to improve the performance of PET.[11–16] Because of the poor compatibility of clay with PET, up to now, it is very difficult to produce exfoliated PET/clay nanocomposite.

Polyamide 6 (PA6) has better compatibility with clay, exfoliated PA6/clay nanocomposites could be prepared easily from *in situ* polymerization or by melt compounding.[17–19] If the PA6 molecular chain could be introduced into PET, the compatibility of clay with PET could be improved, thus the exfoliated PET/clay nanocomposite perhaps could be prepared easily from *in situ* polymerization. In this paper, PET/PA6 copolymer/MMT nanocomposite was synthesized through *in situ* polymerization, the structure and properties of this PET/PA6 copolymer/MMT nanocomposite were studied in detail.

EXPERIMENTAL

Materials

Sodium-MMT with a cation exchange capacity of 100 mequiv/100 g and a nominal particle size of 40 μm was obtained from Hailiang Clay Mineral Corp., Zhejiang, China. ε-Caprolactam, ethylene glycol (EG), 6-aminocaproic acid, and polyvinylpyrrolidone (PVP) were purchased from Beijing Chemical Reagents Company (China). Dimethyl terephthalate (DMT) was a commercial product from Mitsubishi Chemical (Japan).

Preparation of organo-MMT[20]

A suspension of 1 part by weight of sodium-MMT in 40 parts by weight of distilled water, in which 1 part

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by weight of PVP was dissolved, was stirred violently. The temperature was maintained at 90 °C for 4 h. Then the precipitate was filtered and washed thrice with distilled water. The acquired MMT was dried in vacuum to a constant weight at 80 °C and was then ground into powder.

Synthesis of PET/MMT nanocomposite

Two parts by weight of organo-MMT powder was dispersed uniformly in 100 parts by weight of DMT, 72 parts by weight of EG, and zinc acetate catalyst. The mixture was heated to about 180 °C, whereupon methanol was generated. After theoretical amount of methanol was removed, antimony trioxide catalyst was added to the reaction system and the pot temperature was increased to about 280 °C. At the same time, vacuum was applied (<0.1 mmHg) to produce PET/MMT nanocomposite. The content of MMT in PET/MMT nanocomposite is 2%.

Synthesis of PA6/MMT nanocomposite

Two parts by weight of organo-MMT, 95 parts by weight of ε-caprolactam, and 5 parts by weight of 6-aminocaproic acid were placed into a reactor vessel. The mixture was heated to about 90 °C, and stirred violently for 4 h. Then the temperature was increased to about 260 °C, whereupon water was generated. After 6 h later, the PA6/MMT nanocomposite was obtained. The content of MMT in PA6/MMT nanocomposite is 2%.

Synthesis of PA6/MMT master batch

Twenty parts by weight of organo-MMT, 80 parts by weight of ε-caprolactam, and 5 parts by weight of 6-aminocaproic acid were placed into a reactor vessel. The mixture was heated to about 90 °C, and stirred violently for 4 h. Then the temperature was increased to about 260 °C, whereupon water was generated. The PA6/MMT master batch was obtained after 4 h. The content of MMT in PA6/MMT master batch is 20 wt %.

Synthesis of PET/PA6 copolymer/MMT nanocomposite

Ninety parts by weight of DMT, 65 parts by weight of EG, and zinc acetate catalyst were placed into a reactor vessel. The mixture was heated to about 180 °C, whereupon methanol was generated. After the theoretical amount of methanol was removed, 10 parts by weight of PA6/MMT master batch was added to the reaction system. The PA6/MMT master batch was dissolved gradually in reaction system, then antimony trioxide catalyst was added to the reaction system and

the pot temperature was increased to about 280 °C. At the same time, vacuum was applied (<0.1 mmHg) to produce PET/PA6 copolymer/MMT nanocomposite. The content of MMT and PA6 in PET/PA6 copolymer/MMT nanocomposite is 2 and 8 wt %, respectively, according to the feed ratio.

Measurements

Nuclear magnetic resonance

The samples for ^{1}H NMR spectroscopy (~80 mg) were dissolved in D_2SO_4 (2 mL). These solutions were kept at ambient conditions for 5 h so that the selective degradation of the PET units could take place. After this time, a slight opacity of the D_2SO_4 solution was observed in the neat PET sample. By means of centrifugation, minor amounts of white powder were removed, thus obtaining a seemingly transparent solution. All ^{1}H NMR spectra were recorded on a Bruker DMX-4000 apparatus operating at 400 MHz, at 20 °C, using 5 mm o.d. sample tubes. Tetramethylsilane was used as the external standard and was placed in a coaxial 1 mm o.d. capillary. The sequence length of PA6 ($\bar{L}_{PA6}$) was calculated according to the literature.[21]

X-ray diffraction

In Saritzkey–Golay's mode, X-ray diffraction (XRD) was performed at room temperature using a Ragaku Model D/max-2B diffractometer, with Cu Kα radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 100 mA. Testing data were collected from 1.5° to 40° at a scanning rate of 2°/min.

Differential scanning calorimeter

A Perkin–Elmer DSC-7 differential scanning calorimeter thermal analyzer was used for DSC analysis. Each sample about 8 mg was accurately weighted before being placed in DSC span. Under nitrogen atmosphere, it was heated from room temperature to 300 °C with a heating rate of 20 °C/min. The sample was kept for 10 min at this temperature to eliminate the thermal history before cooling at 20 °C/min.

Dynamic mechanical analysis

DMA measurements were performed with a Perkin–Elmer DMA-7 (USA).The experiments were carried out using the three-point-blending geometry over a temperature range of 0–120 °C at a rate 5 °C/min under nitrogen flow. All the samples were analyzed at a constant frequency of 1 Hz, a dynamic force 30 mN, and a static force 33 mN. The rectangular specimen dimensions were $15 \times 2 \times 2$ mm^2.[3]
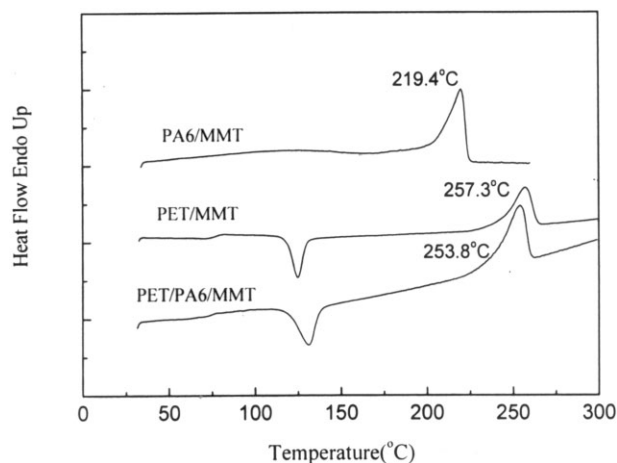
Figure 1 DSC heating thermograms of PA6/MMT nanocomposite (2 w t%), PET/MMT nanocomposite (2 wt %), and PET/PA6 copolymers/MMT nanocomposite (2 wt %).

Transmission electron microscope

The samples were ultrathin-sectioned using a microtome equipped with a diamond knife in a liquid nitrogen trap. The thin sections were 60–100 nm thick. Transmission electron micrographs were obtained with a JEOL-100CX using an acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

The DSC heating thermograms of PA6/MMT nanocomposite, PET/MMT nanocomposite, and PET/PA6 copolymer/MMT nanocomposite are shown in Figure 1. PET/PA6 blends usually have two melting peaks, which are almost identical to those of the neat PET and PA6. PET/PA6 copolymer only has one melting peak, which is between the melting temperature of PA6 and that of PET.[21] The DSC result (Fig. 1) shows that all samples has one endothermic peak, and the melting temperature of PET/PA6 copolymers/MMT nanocomposite is 253.8 °C, which is between the melting temperature of PA6/MMT nanocomposite and that of PET/MMT nanocomposite. This result proved that the nanocomposite synthesized here was PET/PA6 copolymer/MMT nanocomposite, the PA6 molecular chain had been introduced into PET from the ester–amide exchange reaction at the higher polycondensation temperature.

Qi et al.[22] reported that MMT could act as heterogeneous nuclei of PET, and this accelerated the rate of crystallization of PET greatly. DSC cooling scans at a rate of 20 °C/min of PA6/MMT nanocomposite, PET/MMT nanocomposite, and PET/PA6 copolymers/MMT nanocomposite are shown in Figure 2. An exothermic peak occurs at T_{CP} (crystallizing peak temperature) = 173.6, 209.6, and 191.5 °C for PA6/MMT nanocomposite, PET/MMT nanocomposite, and PET/
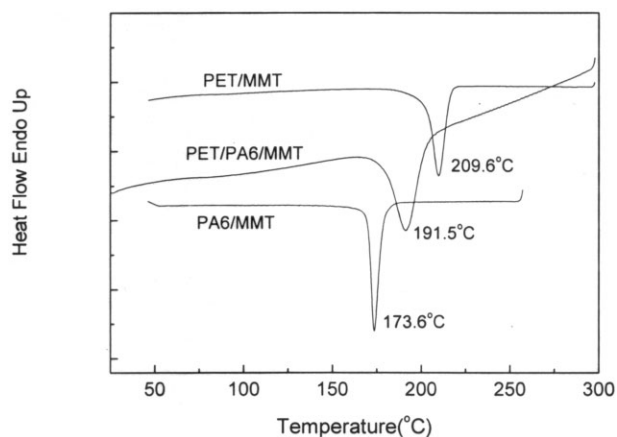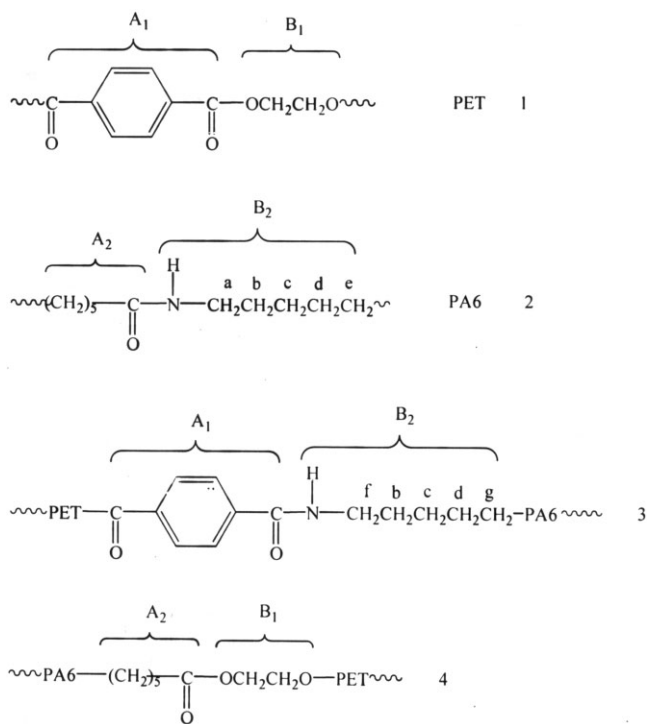

Figure 2 DSC cooling scans of PA6/MMT nanocomposite (2 w t%), PET/MMT nanocomposite (2 w t%), and PET/PA6 copolymers/MMT nanocomposite (2 w t%).

PA6 copolymers/MMT nanocomposite, respectively. The crystallization temperature of PET/MMT nanocomposite was increased markedly compared with that of pure PET. The larger T_{CP} values of PET/MMT nanocomposite indicate that the rate of crystallization increased with addition of MMT. This result is the same with that of former reports.[22] PET/PA6 copolymers/MMT nanocomposite has only one exothermic peak at 191.5 °C, which is between the T_{CP} of PA6/MMT nanocomposite and that of PET/MMT nanocomposite. The order of PET molecular chain was disturbed due to the introduction of PA6 molecular chain introduced into PET; thus, the rate of crystallization of PET/PA6 copolymers/MMT nanocomposite was decreased compared with that of PET/MMT nanocomposite.

The loss tangent (tan δ) and temperature spectra of the nanocomposites are shown in Figure 3, which
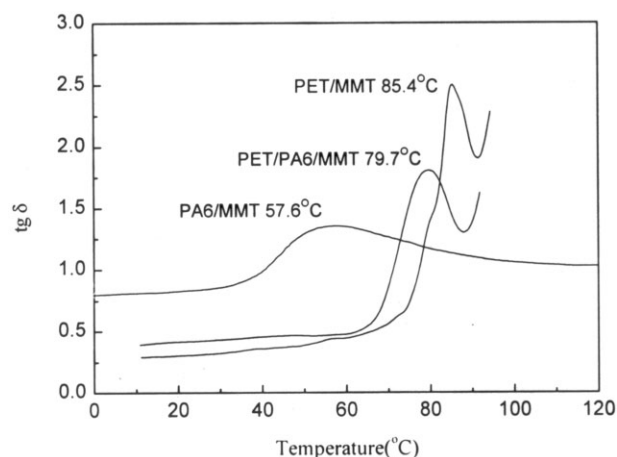
Figure 3 The loss tangent (tan δ)of the nanocomposites as a function of temperature (a) PA6/MMT nanocomposite, 2 wt %; (b)PET/MMT nanocomposite, 2 wt %; (c) PET/PA6 copolymers/MMT nanocomposite, 2 wt %.

Scheme 1. Schematic representation of all chemical structures appearing in PET/PA6 copolymers.

shows that PET/PA6 copolymers/MMT nanocomposite has only one glass transition temperature (T_g) at 79.7 °C, which is between the T_g of PA6/MMT nanocomposite and that of PET/MMT nanocomposite; these results also prove that the nanocomposite synthesized here is PET/PA6 copolymers/MMT nanocomposite, not the PET/PA6 blends/MMT nanocomposite.

All the chemical structures in PET/PA6 copolymer are given in Scheme 1.[21]

The ^{1}H NMR spectra of PET/PA6 copolymer is shown in Figure 4.

^{1}H NMR (D_2SO_4) of PET/PA6 copolymer: d = 1.255–1.346 ($A_2B_2H^c + A_1B_2H^c$), 1.520–1.6664 (H^d +

H^b of A_2B_2 and of A_1B_2), 2.469 ($A_2B_2H^e$), 2.734 ($A_1B_2H^g$), 3.320 ($A_2B_2H^a$), 3. 601 ($A_1B_2H^f$).

The number average sequence lengths of the PA 6 ($\bar{L}_{PA6}$) blocks can be derived from the following expressions[21]

$$\bar{L}_{PA6} = \frac{[A_2B_2H^a]}{[A_1B_2H^f]} + 1 \qquad (1)$$

where $[A_2B_2H^a]$ and $[A_1B_2H^f]$ are the integral intensities of the proton a and proton f.

The PA6 sequence length derived from eq. (1) is 3.75. The results of ^{1}H NMR also proves that the ester–amide exchange reaction had taken place; the average 3.75 repeat units of PA6 are dispersed randomly in the PET molecular chain.

The X-ray diffraction patterns of original MMT, organo-MMT, PET/MMT nanocomposite, and PET/PA6 copolymers/MMT nanocomposite are showed in Figure 5. The XRD pattern of original MMT contains a peak at $2\theta = 7.2°$, while organo-MMT shows a peak at $2\theta = 2.8°$, which are basal reflection from the silicate layers. The gallery distance can be calculated using the Bragg equation, and is found to be 1.2 nm for original MMT and 3.2 nm for the organo-MMT; these results indicate that PVP molecules had intercalated into the galleries of MMT. Increasing of layer distance will weaken the interaction between MMT layers and will facilitate the exfoliation of MMT layers during synthesis and processing.

The compatibility of organo-clay with matrix is of great importance to form a uniform nanocomposite. PET has poorer compatibility with clay, it is very difficult to produce exfoliated PET/clay nanocomposite from *in situ* polymerization. Figure 5 shows that there is still a peak at 2θ angle of 3.8° for PET/MMT nanocomposite; the layer distance is 2.4 nm, according to Bragg's equation, which means that the PET/MMT nanocomposite is a intercalated nanocomposite. There was no peak in low angle region for PET/PA6 copolymers/MMT nanocomposite. It means that the com-
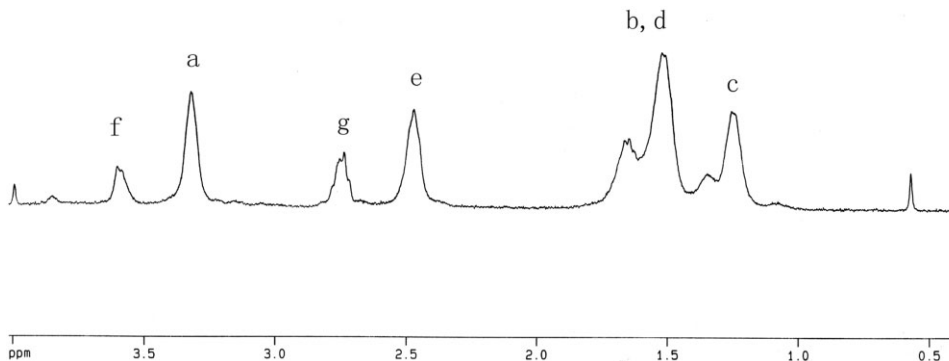
Figure 4 ^{1}H NMR spectra of PET/PA6 copolymer.
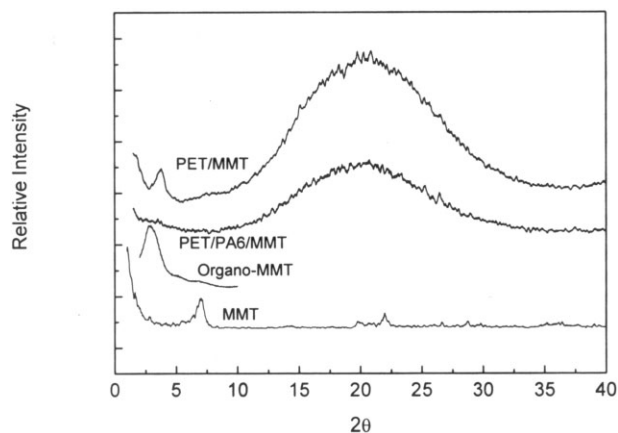
Figure 5 XRD patterns of MMT, organo-MMT, PET/MMT nanocomposite (2 wt %), and PET/PA6 copolymers/MMT nanocomposite (2 wt %).

patibility of PET with clay was improved after the introduction of PA6 molecular chain into PET, thus the layer distance (>5.9 nm) was further expanded, and the dispersion of MMT was improved markedly.

Figure 6 is the TEM image of PA6/MMT master batch and PET/PA6 copolymers/MMT nanocomposite. From Figure 6(a), it could be clearly observed that

organo-MMT layers were dispersed in PA6 matrix uniformly. MMT layers still show a regular face to face style with expanded layer distance. Compared with Figure 6(a), the interlayer space of MMT in PET/PA6 copolymers/MMT nanocomposite has been further expanded [Fig. 6(b)], the layer distance is about 10 nm, which is consistent with the results of XRD. The results of TEM also prove that the dispersion of MMT was improved observably after the introduction of PA6 molecular chain into PET.

CONCLUSIONS

A PET/PA6 copolymers/MMT nanocomposite was prepared by *in situ* polycondensation. The melting temperature, the crystallization temperature, and glass transition temperature of PET/PA6 copolymers/ MMT nanocomposite located between those of PA6/ MMT nanocomposite and PET/MMT nanocomposite. The results of ^{1}H NMR also proved that the ester–amide exchange reaction had taken place; the average 3.75 repeat units of PA6 are dispersed randomly in the PET molecular chain. The results of XRD and TEM proved that the compatibility of PET with clay was increased after the introduction of PA6 molecular
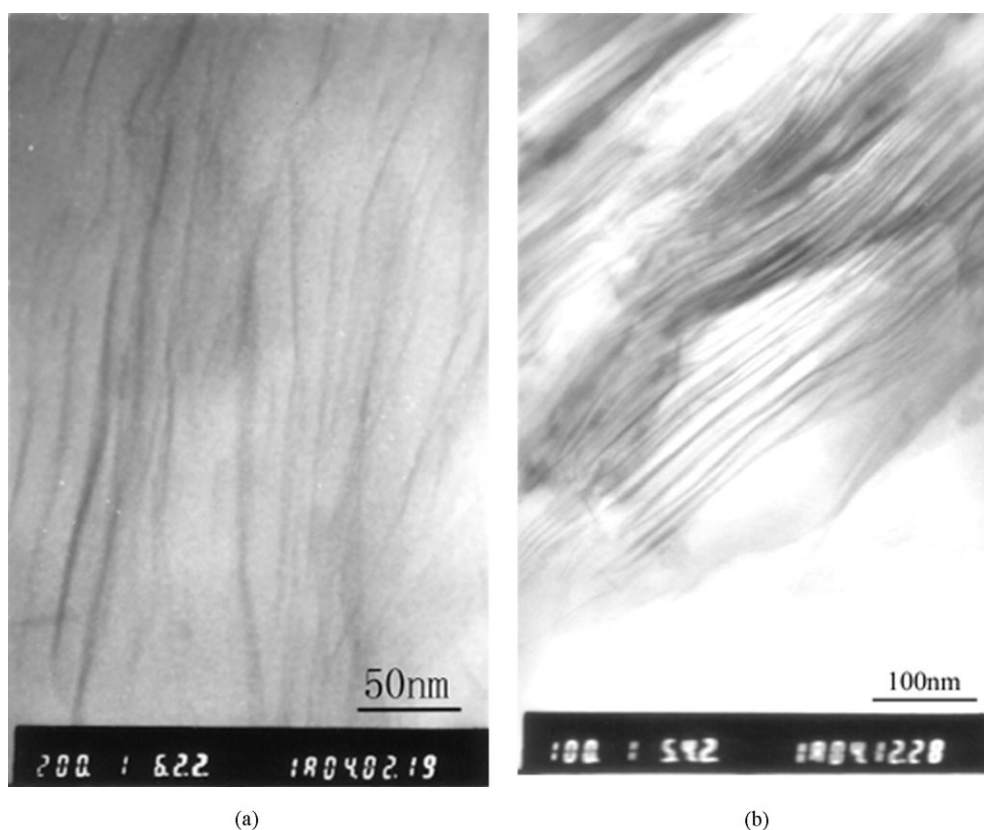
Figure 6 TEM images of PA6/MMT master batch and PET/PA6 copolymers/MMT nanocomposite (a) PA6/MMT master batch; (b) PET/PA6 copolymers/MMT nanocomposite.

chain into PET, and thus the dispersion of MMT in PET/PA6 copolymer was improved observably.

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