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Preparation and characterization of poly(butylene terephthalate) nanocomposites from thermally stable organic-modified montmorillonite

Junfeng Xiao [a,b], Yuan Hu [a,*], Zhengzhou Wang [a], Yong Tang [a], Zuyao Chen [b], Weicheng Fan [a]

[a] *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China*

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Abstract

In this paper, cetyl pyridium chloride (CPC) was employed to modify the montmorillonite. TGA analysis shows that the organic modified clay has higher thermal stability than hexadecyl trimethyl ammonium chloride modified montmorillonite and is suitable to be used for preparing poly(butylene terephthalate) (PBT)/clay nanocomposites at the high temperature. And then PBT/clay nanocomposites were prepared by direct melt intercalation. The results of XRD, TEM and HREM experiments show the formation of exfoliated-intercalated structure. The thermal stability of the nanocomposites does not evidently decrease, but the char residue at 600 °C remarkably increase compared with pure PBT. DSC results indicate that clay improves the melting temperature, the crystallization rate and crystallinity of the PBT molecules in the nanocomposites.

Keywords: Poly(butylene terephthalate) (PBT); Cetyl pyridium chloride (CPC); Nanocomposites; TGA; DSC

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1. Introduction

Since a nylon-6/clay hybrid material reported by the Japanese industrial research group [1] and melt-mixing method without the use of organic solvents used by Giannelis et al. [2], polymer clay nanocomposites have attracted a remarkably strong attention of academic and industrial researchers. From fundamental science viewpoint, the two kinds of nanocomposite structure, intercalated and exfoliated morphologies, respectively offer well-defined model systems with macroscopic quantities of 1–2 nm thin confined polymer films and polymer brushes [3]. From an industrial viewpoint, the dispersion of these ultra-thin (1 nm) ultra-high surface-area fillers in polymers concurrently improves many properties of the materials, namely mechanical, thermal, barrier, and solvent resistance, and also provides a flame retardant character [4].

Poly(butylene terephthalate) (PBT) is an important semicrystalline engineering thermoplastic with many valuable properties including a high rate of crystallization, good solvent resistance, thermal stability, and excellent

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[*] Corresponding author. Tel.: +86 551 3601664/7643; fax: +86 551 3601664.
E-mail address: yuanhu@ustc.edu.cn (Y. Hu).

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processing properties. However, pure PBT has low impact strength and heat distortion temperature. As a reinforced method, PBT/clay nanocomposites have been prepared by polymer melt intercalation [5,6] and in situ intercalative polymerization [7,8] using alkyl ammonium modified montmorillonite. But for PBT nanocomposites, the high temperature, which is required for melt intercalation and bulk processing, generally induces the decomposition of alkyl ammonium cations in the organic-modified montmorillonites [9]. It not only alters the interface between the filler and the matrix polymer, but also induces the degradation of the polyester [10]. Therefore high heat stability of organoclays is needed for the good dispersion of clay in the matrix polymer.

In this paper, we employed cetyl pyridium chloride (CPC) to prepare the thermally stable organic-modified montmorillonites (OMT-CPC) and then prepared PBT/OMT-CPC nanocomposites via direct melt intercalation method. The thermal properties of the nanocomposites were studied compared with those of the pure PBT and PBT/OMT-C16 nanocomposites.

2. Experimental

2.1. Materials

The PBT used in this study was manufactured from Nantong Synthetic Material Plant (PBT1097, density = 1.31 ± 0.02, intrinsic viscosity = 0.97 ± 0.02). The original purified sodium montmorillonite (MMT, with a cation exchange capacity of 96 meq/100 g) and hexadecyl trimethyl ammonium chloride modified montmorillonite, OMT-C16, were kindly provided by Keyan Company. Cetyl pyridium chloride (CPC) was purchased from Shanghai Chemicals with purity greater than 99%.

2.2. The preparation of OMT-CPC

The CPC modified montmorillonites were prepared by a cation-exchange reaction of Na^+ and CPC (equivalent ratio of clay: CPC = 1:1). Five grams of MMT and 1.72 g of CPC were added to 400 mL-distilled water in a 500 mL flask. The mixture was stirred vigorously for 5 h at 80 °C, before the CPC-exchanged silicates were collected by filtration. The solids were subsequently washed with hot distilled water and filtered, until an $AgNO_3$ test indicated the absence of halide anions. The product was placed in a vacuum drying oven at 80 °C for 12 h and then ground to obtain the OMT-CPC.

2.3. The preparation of PBT-clay nanocomposites

The clay and the PBT pellets were dried under vacuum at 80 °C for at least 10 h before use. PBT was melt-mixed with clay in a twin-roll mill (XK-160, made in Jiangsu, China) for 10 min. The temperature of the mill was maintained at 230 °C and the roll speed was 100 rpm. The samples are identified in Table 1.

Table 1
Sample identification and composition

Sample	Composition
PBT1	PBT + MMT (3 wt%)
PBT2	PBT + OMT-C16 (3 wt%)
PBT3	PBT + OMT-CPC (3 wt%)

2.4. Characterization

Infrared spectra were recorded on a Nicolet MAGNA-IR750 spectrometer by the standard KBr disk method in the range of 350–4000 cm^{-1} with a resolution of 4 cm^{-1}.

The dispersibility of the silicate layers in the PBT was evaluated using X-ray diffractometry (XRD), high-resolution electron microscopy (HREM) and bright field transmission electron microscopy (TEM). Films (1 mm) of the nanocomposites were pressed at 230 °C for the XRD measurements. X-ray diffraction experiments were performed at room temperature on a Japan Rigaku D/max-rA X-ray diffractometer (30 kV, 10 mA) with Cu Kα (λ = 1.54178 Å) irradiation at the rate of 2°/min in the range of 1.5–10°. TEM and HREM specimens were cut from epoxy blocks with the nanocomposites powders embedded, at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife. Thin specimens, 50–80 nm, were collected in a trough filled with water and placed on 200 mesh copper grids. HREM images were obtained by JEOL 2010 with an acceleration voltage of 200 kV. TEM images were obtained on a JEOL JEM- 100SX microscope with an acceleration voltage of 100 kV.

Thermogravimetric analyses (TGA) were carried out using a Netzch STA-409c thermal analyzer under nitrogen flow at the rate of 10 °C /min. Differential Scanning Calorimetry (DSC) was carried out on a Perkin Elmer DSC7 under continuous nitrogen flow. The cyclic heating and cooling scans were performed between 50 and 250 °C with a heating/cooling rate of 10 °C/min with retention time of 3 min at 250 °C. The melting and crystallization temperatures were defined at the maxima of the DSC peaks.

3. Results and discussion

3.1. Characterization and thermal analysis of OMT-CPC

Fig. 1 gives the FTIR spectra of CPC, MMT and OMT-CPC. The spectrum of OMT-CPC contains the