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Poly(butylene terephthalate)/Clay Nanocomposites directly Prepared from Pristine Montmorillonite (MMT)

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Summary

Poly(butylene terephthalate) (PBT)/clay nanocomposites have been prepared by melt intercalation method directly from pristine montmorillonite (MMT), using cetyl pyridinium chloride (CPC) as the polymer/clay reactive compatibilizer. The effect of the reactive compatibilizer (CPC) proportion relative to the clay on the structure and properties of the PBT/clay nanocomposites was studied by XRD, TEM, TGA and cone calorimeter. The results show that such appropriate proportion as 1 wt % CPC to 3 wt % MMT induces well-dispersed intercalated morphology and better thermal and flame retarded properties. At last the intercalation mechanism of the technology was discussed.

Introduction

Polymer/clay nanocomposites, as a very promising alternative to conventional filled polymers, have attracted considerable attention of academic and industrial researchers in recent decades. The dispersion of these ultra-thin (1nm) ultra-high surface-area clay layers (usually less than 10 wt %) within a polymer matrix leads to nanocomposites exhibiting markedly improved physicochemical properties, such as higher strength and modulus, better dimensional and thermal stabilities, higher heat distortion temperature and chemical stability, as well as more efficient gas barrier properties and flame retardancy, compared with pure polymers or conventional microcomposites [1, 2].

Poly(butylene terephthalate) (PBT) is an important commercially available semicrystalline engineering thermoplastic with many valuable properties including a high rate of crystallization, good solvent resistance, thermal stability, and excellent processing properties. However, pure PBT has low impact strength and heat distortion temperature. As a reinforced method, PBT/clay nanocomposites have been prepared by melt intercalation [3-5] and in-situ intercalative polymerization [6, 7]. To facilitate the interaction of silicate layers with PBT, organically modified clays were all used in these techniques. But the modification of clay is a tedious process with wasting lots of distilled water.

In this article, a convenient method [8] was used to prepare PBT/clay nanocomposites by melt intercalation starting directly from pristine Na^+ montmorillonite, using cetyl pyridinium chloride (CPC) as the polymer/clay reactive compatibilizer. The thermal and flammability properties of the nanocompoistes were compared with pure PBT, and the mechanism of this method was studied.

Experimental

Materials

The PBT (PBT1084, density=1.31±0.02, intrinsic viscosity=0.84±0.02)used in this study was obtained from Nantong Xingchen Synthetic Material Co. Ltd. The original purified sodium montmorillonite (MMT) with a cation exchange capacity of 96 meq/100g and an interlayer spacing of d_{001}=15.1 Å was used as the nanofiller precursor. Cetyl pyridinium chloride (CPC) was purchased from Shanghai Chemicals with purity greater than 99%.

The preparation of PBT-clay nanocomposites

MMT, CPC and PBT pellets were dried under vacuum at 80 °C for at least 10 h before use. Firstly, the pristine MMT and different amount of CPC were mixed and ground together in a pestle and mortar, and then the mixed powder (MMT+CPC) were melt-mixed with PBT 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. Table 1 shows the mixing weight ratio of the samples.

Table 1. Summary of PBT/clay composites.

Compound	PBT (wt. %)	MMT (wt. %)	CPC (wt. %)	Main Diffraction Peak (d_{001}) (Å)
B1	97	3		15.1
B2	96.5	3	0.5	33.7
B3	96	3	1	34.6
B4	95	3	2	35.3
B5	94	3	3	34.6

Characterization

The dispersibility of the silicate layers in the PBT was evaluated using X-ray diffractometry (XRD), and bright field transmission electron microscopy (TEM). Films (1mm) of the composites 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 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. TEM images were obtained on by H-800 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.

Combustion property was characterized by cone calorimeter. The signals from the cone calorimeter were recorded and analyzed by a computer system. All samples ($10 \times 10 \times 0.3$ cm^3) were examined in a Stanton Redcroft cone calorimeter according to ASTM 1356-90 under a heat flux of 50kW m^{-2}. The experiments were repeated three times and the results were reproducible to within ±10%. The cone data reported here is the average of three replicated experiments.

Results and discussion

Structure of the PBT-clay nanocomposites

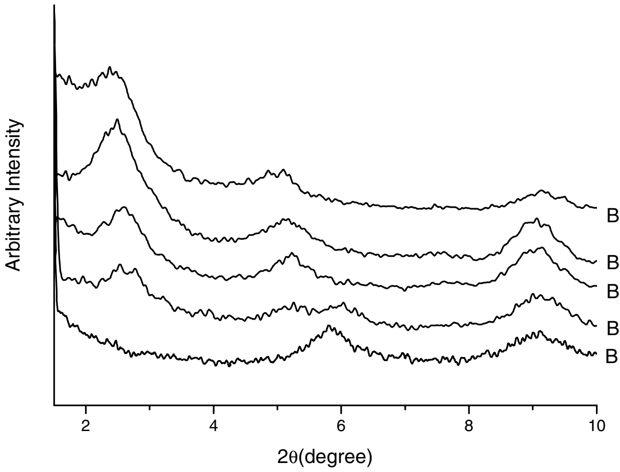

Figure 1. XRD patterns of compounds B1 [PBT+3 wt % MMT], B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)], B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)], B4 [PBT+ (3 wt % MMT+ 2 wt % CPC)], and B5 [PBT+ (3 wt % MMT+ 3 wt % CPC)].

The effect of reactive compatibilizer (CPC) weight proportion relative to the clay on the morphology of the PBT/clay composites was studied. Compounds B1, B2, B3, B4, and B5, filled with the same amount of inorganic (3 wt % MMT) and different amount of CPC (shown in Table 1), were prepared. The XRD results of the compounds are presented in Fig. 1, and the distances of the main diffraction peaks are summarized in Table 1. Compound B1 [PBT+3 wt % MMT] exhibits only a weak peak corresponding to the same interlayer distance of 15.1 Å as that of pristine MMT, which indicates that PBT cannot intercalate into the gallery of MMT without CPC. But there are different results when reactive compatibilizer (CPC) is added. In B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)] with adding only 0.5 wt % CPC, a notable diffraction peak at 33.7 Å as well as an overlapped peak around 40.9 Å coexists with that of pristine MMT. This shows that PBT has intercalated some of clay layers by the aid of CPC. It is especially noted that the peak around 40.9 Å could belong to the peak intercalated by CPC, which did not be intercalated by PBT chains in melt blending. This is consistent with the XRD result of the grinding mixture of MMT (3 wt %) and CPC (1 wt %), as shown latter. However, when CPC is 1 wt % in B3 [PBT+ (3 wt %

MMT+ 1 wt % CPC)], the diffraction peak of MMT and the intercalated peak by CPC disappear, and we get a sharp peak at 34.6 Å with the second diffraction peak. For B4 [PBT+ (3 wt % MMT+ 2 wt % CPC)], the diffraction peak increases a little to 35.3 Å. However, when the content of CPC increases to 3 wt % in B5 [PBT+ (3 wt % MMT+ 3 wt % CPC)], the d_{001} does not increase but decreases slightly. This indicates that the intercalation capability has a certain limit [9].

To further confirm the dispersion of clay in the PBT matrix, TEM measurements were carried out. The TEM micrographs are shown in Fig. 2. For B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)], intercalated tactoids containing many parallel silicate layers and large particles in the micron range can be both observed in Fig. 2a. This is consistent with the XRD result, indicating the gallery of some of clay layers has been intercalated by PBT or CPC and other not. When the content of CPC increases to 1 wt % in B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)], the TEM image (Fig. 2b) shows that large particles in the micron range do not be seen and the distribution of the silicate layers in the PBT matrix is well uniform and ordered. B4 nanocomposite [PBT+ (3 wt % MMT+ 2 wt % CPC)] also present good dispersion of clay, but the size of intercalated tactoids is somewhat larger than B2 nanocomposite in Fig.2c. However, when the content of CPC increases to 3 wt % in B5 nanocomposite [PBT+ (3 wt % MMT+ 3 wt % CPC)], the intercalated tactoids have begun to agglomerate together, as shown in Fig.2d. This indicates that preparation of nanocomposites with well dispersed morphology need the appropriate reactive compatibilizer proportion relative to the clay, and the nanocomposite including 3 wt % MMT and 1 wt % CPC is the best of this experimental series. It is coincident that the appropriate reactive

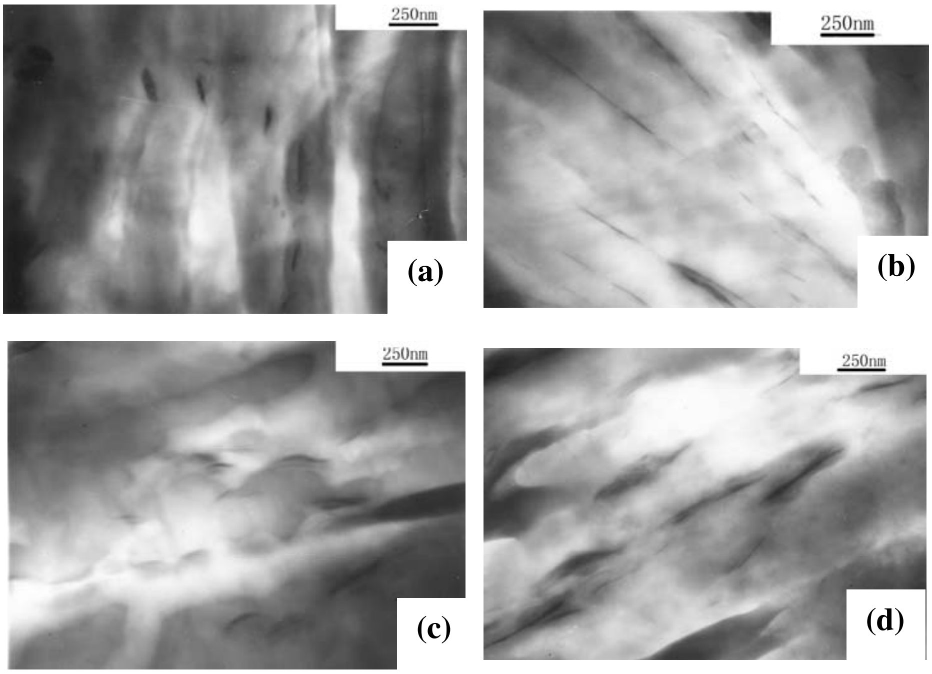

Figure 2. TEM images of PBT/clay nanocomposites: (a) B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)]; (b) B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)]; (c) B4 [PBT+ (3 wt % MMT+ 2 wt % CPC)], and (d) B5 [PBT+ (3 wt % MMT+ 3 wt % CPC)].

compatibilizer proportion relative to the clay approximatively equals to the equivalent ratio by the cation-exchange reaction [5]. The excessive amounts, 2 and 3 wt % CPC, induce the detrimental properties of the nanocomposites. This may be due to the change of orientation of CPC on the surface of clay, which alters the interfacial interaction between clay and PBT chains [10].

Thermal stability

It is reported that the polymer-clay nanocomposites can improve thermal stability of many polymers such as PMMA [11], PS [12]. The reason is that clay layers act as a superior insulator and a mass –transport barrier to the volatile products generated during decomposition for increasing the thermal stability.

The thermal properties of pure PBT and these nanocomposites were analyzed by thermogravimetric analysis (TGA). The TGA curves are shown in Fig. 3. The 3% weight loss temperature ($T_{3\%}$), the maximum decomposition temperature (T_{max}) and char residue at 600°C are listed in Table 2. The results especially char residue at 600°C show that the nanocomposites have higher thermal stability than pure PBT. It should be mentioned that $T_{3\%}$ and T_{max} of nanocomposite B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)] are both smaller than those of B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)]. It is possibly attributed to the present of more amount of volatile organic reactive compatibilizer (CPC).

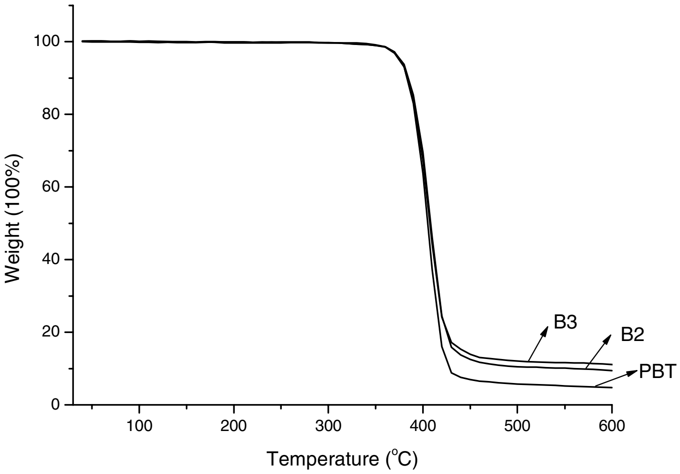

Figure 3. TGA curves of pure PBT, B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)] and B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)].

Table 2. Thermal properties of PBT/clay composites

	$T_{3\%}$ (°C)	T_{max} (°C)	The char residue at 600°C (wt %)
PBT	366.2	406.7	4.71
B2	370.8	409.8	6.79*
B3	369.9	407.3	8.47*

* The char for MMT and CPC at 600°C have already been subtracted.

Flammability properties

Cone calorimetry is one of the most effective bench-scale methods for studying the flammability properties of materials. Characterization of the flammability properties of a variety of polymer/clay nanocomposites, under firelike conditions, using cone calorimetry has elucidated reduced flammability properties for many types of polymer/clay nanocomposites [12-15]. Heat release rate, in particular peak HRR, has been found to be the most important parameter to evaluate fire safety [13].

The heat release rate (HRR) plots for pure PBT, B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)] and B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)] at a heat flux of 50 KW/m^2 were shown in Fig. 4. The peak HRR of B2 decreases 14% compared to pure PBT while that of B3 falls more to 24%. The reason is that clay layers better disperses in B3 than B2.

Moreover, it should be noted that the time to ignite of the nanocomposites are both relatively short in comparison with pure PBT. The initial HRR for the nanocomposites (Fig. 4) are both higher for the first minute following ignition than pure PBT, probably because of thermal decomposition of reactive compatibilizer (CPC) resulting in the formation of volatile combustibles, as shown in Ref. [14].

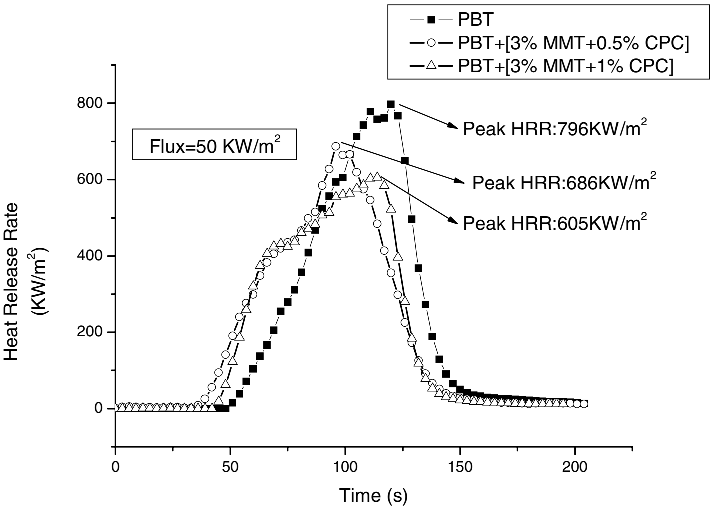

Figure 4. Heat release rate (HRR) of pure PBT, B2 [PBT+ (3 wt % MMT+ 0.5 wt % CPC)], and B3 [PBT+ (3 wt % MMT+ 1 wt % CPC)].

Mechanism of intercalation

Ishida H et al [16] have reported the use of epoxy as the swelling agent of polymer/organoclay hybrids. The mixture of MMT (3 wt %) and CPC (1 wt %) ground for 10 min in a pestle and mortar shows a sharp peak of 39.6 Å with the second, third peaks and a peak of 15.1 Å in Fig. 5. This indicates part of MMT has been intercalated by CPC. So in this paper, CPC serves to modify the clay layers, as well as to swell the clay layers. We deduce the mechanism: at the process of grinding the MMT and CPC together in a pestle and mortar, the CPC surfactant diffuses to the round of clay layers, and then through shear stress and static adsorption some surfactant molecules intercalate into some of the silicate layers and expand them. When the ground mixture is melt-mixed with PBT, the surfactant continues the same

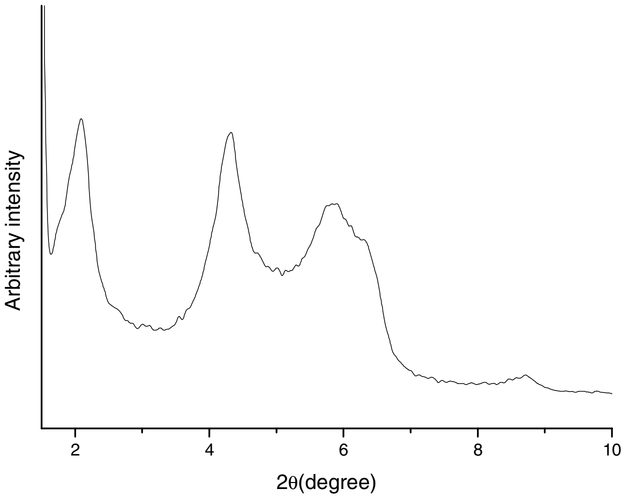

Figure 5. XRD pattern of the mixture of MMT (3 wt %) and CPC (1 wt %) ground for 10 min.

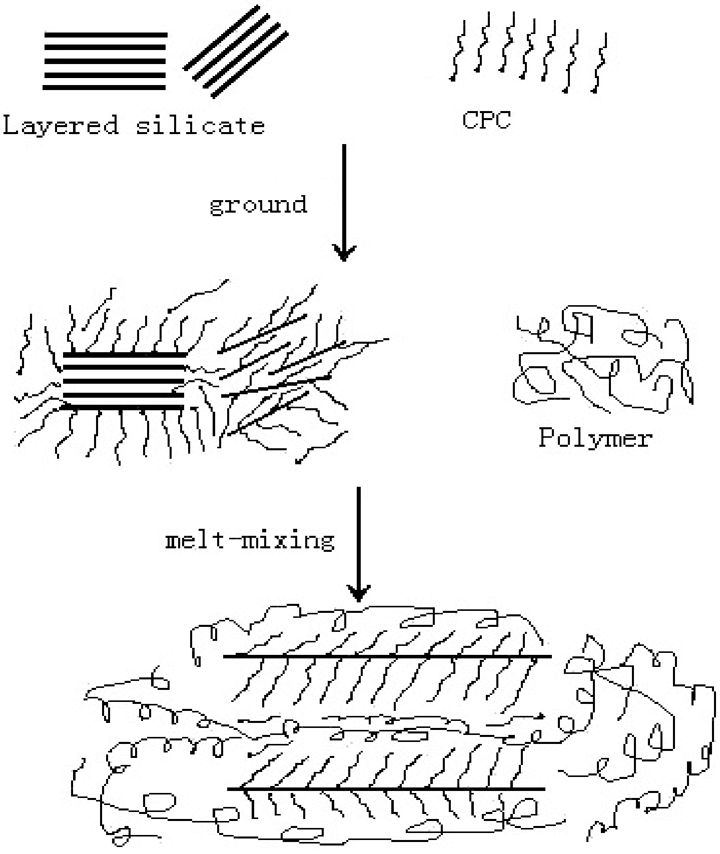

Figure 6. Schematic of intercalation mechanism.

action as that in the grinding process, and acts as a carrier to transport the chains of PBT matrix into the interlayer of clay simultaneously. Schematic of intercalation mechanism has been shown in Fig. 6.

Conclusions

PBT/clay nanocomposites have been successfully prepared by melt intercalation technique directly from pristine Montmorillonite (MMT), using cetyl pyridinium chloride (CPC) as the reactive compatibilizer. Kinds of characterization show that the appropriate proportion of reactive compatibilizer (CPC) to the clay (3 wt % MMT+ 1 wt % CPC) has produced well-dispersed structure and good thermal and flammability properties. At last the supposed mechanism of the technology has been studied.

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