

NOTE

Novel Preparation of Poly(propylene)–Layered Silicate Nanocomposites

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ABSTRACT: We used a novel approach to prepare poly(propylene)–clay nanocomposite starting from pristine montmorillonite and reactive compatibilizer hexadecyl trimethyl ammonium bromide. The nanocomposite structure was revealed by X-ray diffraction and high-resolution electronic microscopy. The thermal properties of the nanocom-

posite were investigated by thermogravimetric analysis. An increase of thermal stability was observed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2586–2588, 2003

Key words: poly(propylene) (PP); nanocomposites; clay

INTRODUCTION

Polymer–nanocomposites have aroused the interest of researchers since the Toyota group reported the *in situ* intercalative polymerization of polyamide 6 (PA6)–nanocomposites.¹ In recent years, many polymer layered silicate nanocomposites (PLSN), such as PA6,^{2,3} poly(methyl methacrylate) (PMMA),^{4, 5} polystyrene (PS),^{6,7} etc. have been synthesized. However, it is difficult to disperse silicate layers of montmorillonite (MMO) at the nanometer level in nonpolar polymers because the silicate layers of clays have polar hydroxyl groups that are incompatible with nonpolar polymers, such as poly(propylene) (PP). To synthesize nonpolar polymer nanocomposites, researchers usually used maleic anhydride (MA),^{8, 9} which can make it possible for polar functional groups to attach to the molecular chain of the polymer. Subsequently, the modified polymer is melt mixed with organomodified clay. In this way, PP–clay nanocomposites have been successfully synthesized. Recently, studies of using MA as a reactive reagent that acts both as a modifying additive for the polymeric matrix and as a swelling agent for the silicate have been reported.¹⁰ PP–clay nanocomposites have also been successfully synthesized. In both of these approaches, researchers organomodified clay and MA.

In this article, we report the use of a novel approach¹¹ to synthesize PP–clay nanocomposite by melt intercalation, using pristine clay and PP instead of organomontmorillonite (OMT) and MA-modified PP (MAPP) or oligomer PP. With

this method, a cationic surfactant, such as an ammonium salt bearing long alkyl chains (C16), is used as the polymer–clay reactive compatibilizer. The aim of our investigation was to provide a general concept for manufacturing polymer nanocomposites by direct melt intercalation.

EXPERIMENTAL

Poly(propylene) (PP; F401) was supplied as pellets by the Yangzi Petrochemical Company (Nanjing, China). The pristine montmorillonite (MMT, with a cation-exchange capacity of 97 meq/100 g) was kindly provided by KeYan Company (Hefei, China). Hexadecyl trimethyl ammonium bromide (C16) was studied as the potential clay–matrix reactive compatibilizer. The general method described in the literature,¹² using OMT, was followed for the purpose of comparison.

Three PP-based compositions (Table I) filled with MMT or OMT were prepared on a two-roll mill (XK-160, JangShu, China) operating at 200°C for 18 min. The three compositions are (1) pristine MMT, (2) OMT, and (3) a mixture of pristine MMT and C16. As for PP–clay nanocomposite, the pristine MMT (dried powder) and C16 were mixed and ground in a mortar with a pestle. During the blending procedure, the mixed powder was directly added to the molten PP, and then the mixture was melt-mixed for ~16 min. The resultant PP–clay nanocomposites were then annealed under vacuum for 12 h at 100°C.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis was carried out (Cu, $\lambda = 1.54178 \text{ \AA}$, $2\theta = 1.5\text{--}10^\circ$) on all the three compounds. The XRD patterns of the compounds are compared in Figure 1.

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TABLE I
PP-Based Composites Filled with Pristine MMT and OMT

Sample	Clay (wt %)	Compatibilizer (C16) (wt %)
1	Pristine MMT (4)	—
2	OMT (4)	—
3	Pristine MMT (4)	2

The d_{001} peak of pristine MMT at $2\theta = 5.8^\circ$ corresponds to 1.4 nm (Figure 1a). Compound 1 exhibits only a weak peak corresponding to an interlayer distance of 1.4 nm (Figure 1b), which is similar to the interlayer distance of the pristine MMT. The interlayer distance of compound 2 is not changed compared with that of OMT (Figure 1d). However, the results are different when reactive compatibilizer C16 is used in hybrids. As seen in Figure 1e, an intercalated morphology is obtained only for compound 3. This morphology is characterized by a main diffraction peak (d_{001}) corresponding to an interlayer distance of 40.06 Å.

Compounds 2 and 3 were examined by high-resolution electronic microscopy (HREM). HREM specimens were cut at room temperature from films of compounds embedded in an epoxy block with an ultramicrotome equipped with a diamond knife (Diatome, Switzerland). HREM images were obtained with a JEOL2010 microscope at an acceleration voltage of 200 kV. Primary particles composed of many silicate layers can be seen in the HREM image of compound 2 (Figure 2a), indicating that there is no intercalation of the polymer between the layers. However, a different behavior is displayed by compound 3. The HREM picture of compound 3 shows a more complex situation. The distance of the interlayer distance is 2.5–4.0 nm, but a variable number of lamellae are seen (Figure 2b). We conclude, therefore, that compound 3 has a mixed nanomorphology.

Thermal stability is an important property in which the nanocomposite morphology plays an important role. Pure PP and compound 3 were analyzed by thermogravimetric

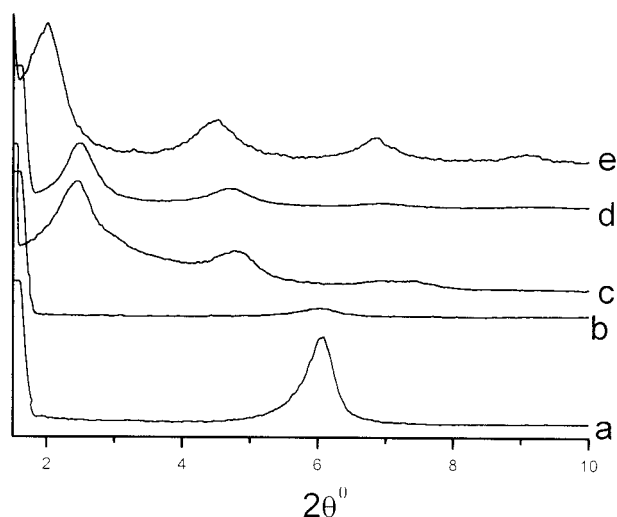
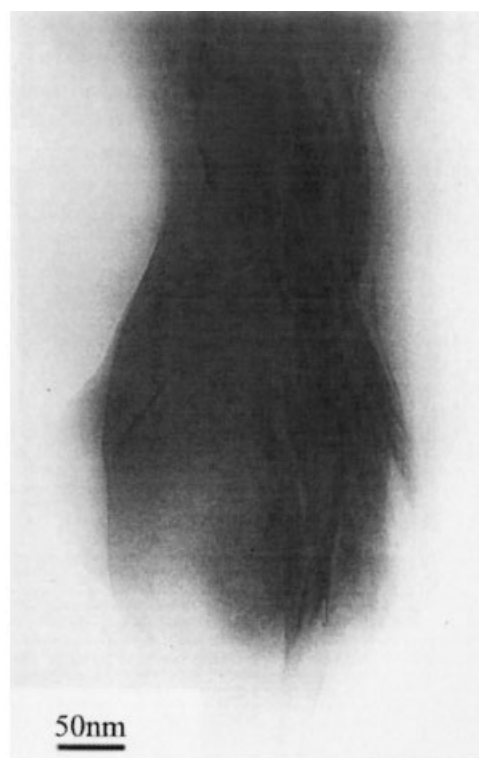
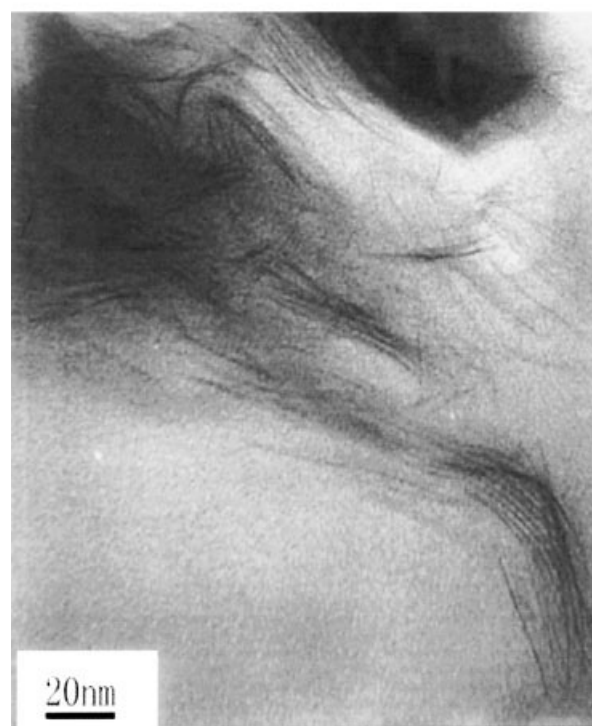


Figure 1 XRD patterns of MMT and PP-MMT hybrids: (a) MMT; (b) PP+MMT (c) OMT; (d) PP+OMT; and (e) PP+MMT+C16.



(a)



(b)

Figure 2 HREM images of PP-clay hybrids: (a) compound 2 (PP+OMT) and (b) compound 3 (PP+MMT+C16).

analysis (TGA) using a Netzsch STA-409c thermal analyzer under nitrogen flow from 25 to 800°C at the rate of 10°C/min. The TG curves are shown in Figure 3. Both the 5% loss

TABLE II
Thermal Properties of PP- and PP-Clay Nanocomposites

Sample	$T_{-5\%}$ (°C)	T_{\max} (°C)
PP	336.4	438.5
PP + MMT + C16	349.2	

temperature ($T_{-5\%}$) and the maximum weight loss temperatures (T_{\max}) are listed in Table 2. The $T_{-5\%}$ temperature of thermodegradation of pure PP is lower than that of compound 3, which is in disagreement with the result reported in the literature.¹⁰ This difference may be because MA was not used in this study. The melting temperature of MA is low, and unreacted MA could be easily sublimed, which could result in the decrease of the onset temperature of thermodegradation of PP-clay nanocomposite. Indeed,

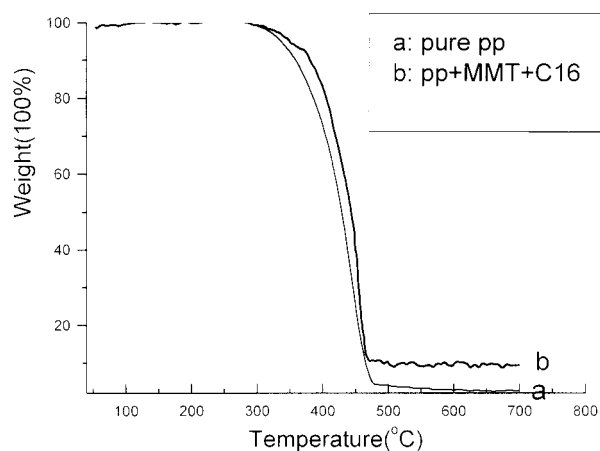


Figure 3 The TG curves for pure PP and compound 3 (PP+MMT+C16).

from Figure 3 we can see that the thermal stability of compound 3 is improved compared with that of pure PP.

CONCLUSION

In this study we used a novel approach to prepare PP-based nanocomposites by melt intercalation. Starting from pristine MMT and by adding a surfactant (C16), this method achieves compatibilization of the clay platelets with the polymer matrix. The nanocomposite structure is evidenced by the XRD and HREM data. Moreover, TGA results indicate that the thermal stability of the PP-clay nanocomposite is improved.

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