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SHORT COMMUNICATION

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Preparation and characterization of nylon 6/Cu^{2+}-exchanged and Fe^{3+}-exchanged montmorillonite nanocomposite

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Abstract Nylon 6/Cu^{2+}-exchanged and Fe^{3+}-exchanged montmorillonite nanocomposites have been prepared by a melt intercalation technique directly from Cu^{2+}-exchanged and Fe^{3+}-exchanged montmorillonite. Hexadecyltrimethylammonium bromide was chosen as the clay/matrix reactive compatibilizer. The intercalation spacing and the degree of dispersion were determined by X-ray diffraction and transmission electron microscopy. Also the thermal character of the nanocomposites prepared was analyzed by thermogravimetric analysis.

Keywords PA6 · Nanocomposites · Cu^{2+}-exchanged and Fe^{3+}-exchanged montmorillonite

Introduction

Recently, much attention has been paid to polymer nanocomposites, especially polymer-layered silicate nanocomposites, which represent a rational alternative to conventional filled polymers. Nanocomposite technology has been described as the next great frontier of material science. Because by employing minimal addition levels (below 10 wt%), nanoclays enhance mechanical, thermal, dimensional and barrier performance properties significantly [1, 2, 3, 4, 5].

Traditionally, in order to facilitate the interaction of silicate layers with a polymer, the clay is modified with an alkylammonium salt (surfactant molecule) by a cation-exchange reaction, because the alkylammonium makes the hydrophilic clay surface organophilic. However, preparation of polymer/clay nanocomposites starting directly from natural (Na^+ base) clay while using an ammonium salt bearing long alkyl chains as a polymer/clay reactive compatibilizer is also a possible method [6, 7]. This work aimed at the synthesis of a nylon 6 (PA6)/Cu^{2+}-exchanged and Fe^{3+}-exchanged montmorillonite (Cu^{2+}-MMT, Fe^{3+}-MMT) nanocomposite by this new method. The significance of this work lies in the many types of nanocomposites that can be prepared. Moreover, the as-prepared nanocomposites have fire-retardant potential, because Cu^{2+} and Fe^{3+} ions can collaborate with some fire retardants to improve the flame-retardant ability of the nanocomposites [8].

Experimental

Materials

PA6(1003NW8) was supplied as pellets by UBE Company, Japan. The original purified sodium montmorillonite (MMT, with a cation-exchange capacity of 96 mEq/100 g and an interlayer spacing $d_{001} = 13$ Å) and organophilic montmorillonite (OMT) were kindly provided by Keyan Company. OMT was prepared from MMT by an ion-exchange reaction using hexadecyltrimethylammonium bromide (C16) in water according to the reported method [1]. C16 was obtained from Shanghai Chemistry Company.

Cu^{2+}-MMT and Fe^{3+}-MMT were prepared by stirring MMT in a solution of 0.1 M $CuSO_4$ or $FeCl_3$, respectively, for 3 h. The resulting material was washed with distilled water and then centrifuged until a negative test for SO_4^{2-} (Cu^{2+} clay) or Cl^- (Fe^{3+} clay) was obtained [9].

The preparation of PA6/clay hybrid

Samples were prepared by firstly grinding 5 wt% ion-exchanged clay and 2.5 wt% C16 together thoroughly, and then, melt-mixing with 92.5 wt% PA6 at 245 °C using a twin-screw mill (XK-160, China) for 10 min to yield hybrids.

Evaluation of dispersibility of the clay in a polymer matrix

The dispersibility of the silicate layers in the PA6 was evaluated using X-ray diffraction (XRD) and bright field transmission electron microscopy (TEM). XRD experiments were performed at room temperature using a Japan Rigaku D/max-rA X-ray diffractometer (30 kV, 10 mA) with Cu ($\lambda = 1.54178$ Å) irradiation at the rate of 2°/min in the range of 1.5–10°. TEM specimens were cut from an epoxy block with the embedded PA6 nanocomposites at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife. TEM images were obtained using a JEOL JEM-100SX with an acceleration voltage of 100 kV.

Thermal analyses

The thermal property of the PA6/Cu^{2+}-MMT and Fe^{3+}-MMT nanocomposites was investigated by thermogravimetric analysis (TGA), which was performed with a Netzsch STA-409C under an N_2 atmosphere at a rate of 10 °C/min.

Result and discussion

Dispersibility of PA6/Cu^{2+}-MMT and Fe^{3+}-MMT nanocomposite

The XRD patterns of MMT, OMT, Fe^{3+}-MMT, Cu^{2+}-MMT, PA6/OMT, PA6/Fe^{3+}-MMT/C16, and PA6/Cu^{2+}-MMT/C16 are shown in Fig. 1. The results of the XRD patterns for these nanocomposites are shown in Table 1. The peaks correspond to the (001) plane reflections of the clays. The average basal spacing of MMT increases by organic modification from 1.3 to 2.2 nm, when original MMT is modified by C16. These increased spacings suggest the chain of C16 intercalates into the gallery of MMT and expands it [2]. The broadening of the d_{001} peak of PA6/OMT, PA6/Fe^{3+}-MMT/C16, and PA6/Cu^{2+}-MMT/C16 shows an intercalated–delaminated structure in these nanocomposites. Though the ion-exchanged MMTs were not modified by C16 before being intercalated with PA6, but were ground together with C16, as-prepared nanocomposites had a similar structure as the nanocomposite prepared by melt-mixing of OMT and PA6. The conclusion can also be drawn from the TEM photographs of PA6/OMT, PA6/Fe^{3+}-MMT/C16, and PA6/Cu^{2+}-MMT/C16 (Figs. 2, 3, 4). These photographs show that OMT, Fe^{3+}-MMT/C16, and Cu^{2+}-MMT/C16 retain layered structures and dispersed well in PA6, and confirmed the intercalated structures.

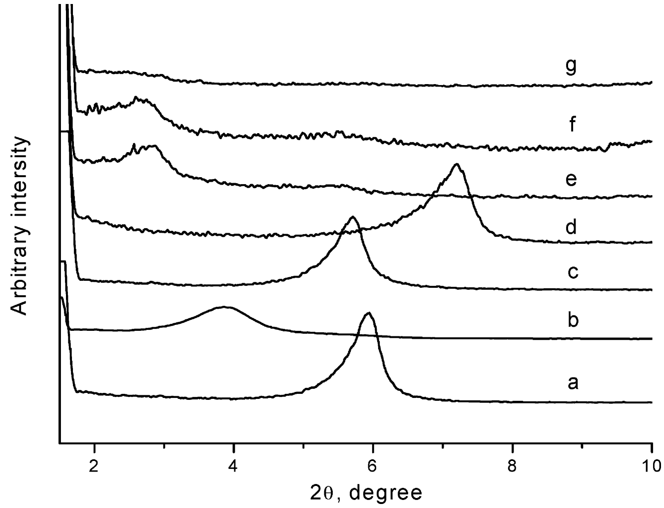

Fig. 1 X-ray diffractions patterns for (*a*) sodium montmorillonite (*MMT*), (*b*) organophilic montmorillonite (*OMT*), (*c*) Fe^{3+}-MMT, (*d*) Cu^{2+}-MMT, (*e*) nylon 6(*PA6*)/OMT, (*f*) PA6/Fe^{3+}-MMT/C16, and (*g*) PA6/Cu^{2+}-MMT/C16

Thermal degradation of PA6/clay nanocomposite

The TGA results of virgin PA6, PA6/OMT, PA6/Fe^{3+}-MMT/C16, and PA6/Cu^{2+}-MMT/C16 are shown in Fig. 5. The thermal stability of the PA6/ion-exchanged clay/C16 will be discussed and compared with the virgin PA6 and PA6/OMT, respectively. The thermogravimetric analyses were made at a rate of 10 °C/min to measure three parameters: the onset temperature of thermal degradation (T_{onset},we designated the onset point as 5 wt% weight loss), the middleweight loss temperature ($T_{0.5}$, we designated the middleweight point as 50 wt% weight loss), and the charred residue at

Table 1 Main diffraction peak (d_{001}). Sodium montmorillonite (*MMT*), organophilic montmorillonite (*OMT*), nylon 6 (*PA6*), hexadecyltrimethylammonium bromide (*C16*)

	MMT	OMT	Fe^{3+}-MMT	Cu^{2+}-MMT	PA6/OMT	PA6/Fe^{3+}-MMT/C16	PA6/Cu^{2+}-MMT/C16
d_{001} (nm)	1.3	2.2	1.56	1.23	3.1	3.4	3.0

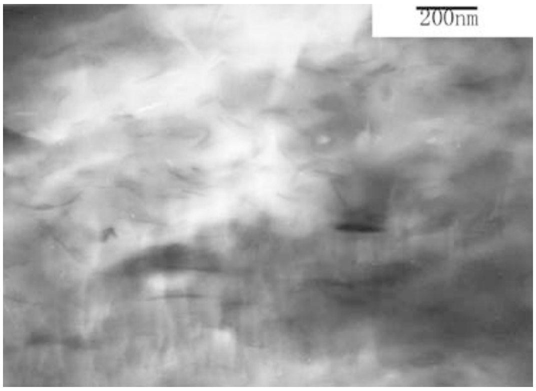

Fig. 2 Transmission electron microscope (*TEM*) image of PA6/OMT nanocomposite

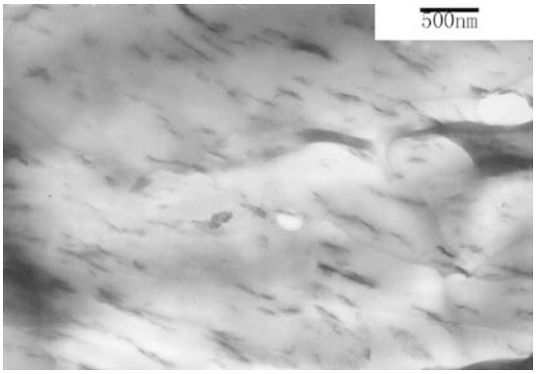

Fig. 4 TEM image of PA6/Cu^{2+}-MMT/C16 nanocomposite

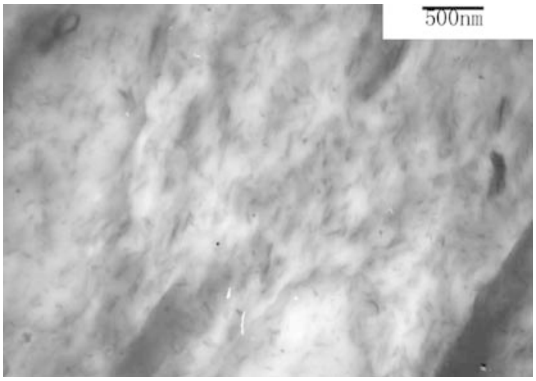

Fig. 3 TEM image of PA6/Fe^{3+}-MMT/C16 nanocomposite

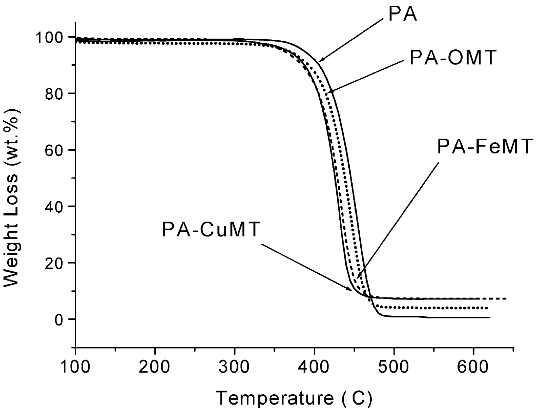

Fig. 5 Thermogravimetric analysis curves of pure PA6, PA6/OMT, PA6/Fe^{3+}-MMT/C16, and PA6/Cu^{2+}-MMT/C16

600 °C. The results are listed in Table 1. From the TGA curves, one can see that when 5 wt% OMT was added to PA6, T_{onset} and $T_{0.5}$ decrease and the charred residue at 600 °C increases. When OMT is substituted with Cu^{2+}-MMT and Fe^{3+}-MMT, the differences become larger. $T_{0.5}$ of PA6/OMT decreases by 7.4 °C and the charred residue at 600 °C of PA6/OMT was improved by 3.7 wt%, respectively, compared to that of PA6. While $T_{0.5}$ of PA6/ion-exchanged MMT/C16 decreases by nearly 10 °C and the charred residue at 600 °C of increases by 3.0 wt% respectively, compared to that of PA6/OMT. These results indicate that the cations of some transition metals (e.g., Cu^{2+}, Fe^{3+}) may decrease the thermooxidative stability of PA6 and increase the charred residue. The effect was attributed to the ability of these cations [10] to form complexes in which the metal atoms are coordinately bonded to the carbonyl oxygen atom of the amide group and are surrounded by polar solvent molecules. PA6 containing metal halides (the metal cations in the galleries of clay can couple with the Br$^-$ in C16 to form metal halides) starts to decompose at a lower temperature than pure PA6; however, it produced a substantially higher solid residue, which indicates extensive involvement of PA6 in the charring processes.

It has been reported [11] that anhydrous FeX_3 (X=Cl$^-$, Br$^-$) shows a catalytic effect on degradation and an impeding effect on the crystallization of PA6. Complexation of Fe^{3+} with the amide group perturbs the hydrogen bonding and results in a decrease inthe crystalline content and an increase in the melt viscosity caused by intrachain and interchain cross-links through the FeCl$_3$. It was also suggested [12] that Fe^{3+} cations facilitate decomposition of hydroperoxides through a reversible Fe$^{3+}\rightleftharpoons$Fe^{2+} oxidative–reductive catalytic process.

Conclusion

This study has demonstrated the ability to prepare PA6-based nanocomposites by melt intercalation starting from Cu^{2+}-MMT and Fe^{3+}-MMT by adding a cation surfactant as a reactive compatibilizer. The morphology of these nanocomposites indicates that as-prepared nanocomposites have a similar intercalated–delaminated structure as PA6/OMT nanocomposite. What interests us most is the catalysis of the transition-metal cations, which can make PA6 decompose at a lower temperature than PA6/OMT and produce more solid residue. More work will be discussed in following papers.

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