Synthesis and Characterization of Poly(methyl methacrylate)/Montmorillonite Nanocomposites by *In Situ* Bulk Polymerization

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ABSTRACT: Poly(methyl methacrylate)/montmorillonite (MMT) nanocomposites were prepared by *in situ* bulk polymerization. The results showed that the silicone coupling agent affected the structure and properties of hybrid materials. XRD analysis showed that the dispersion of clay in nanocomposites with silicone-modified organophilic MMT was more ordered than that in nanocomposites with unmodified organophilic MMT. The glass transition temperature (T_g) of the nanocomposites was 6–15°C higher and the thermal decomposition temperature (T_d) was 100–120°C higher than those of pure PMMA. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2256–2260, 2003

Key words: nanocomposites; poly(methyl methacrylate); *in situ* bulk polymerization; silicone coupling agent

INTRODUCTION

In recent years, there has been great attention to polymer/clay nanocomposites. This is due mainly to these materials exhibiting greatly different physical and chemical properties from a polymer matrix.[1–6] Since the properties of the materials are directly related to the morphology of these systems, the dispersion of the inorganic phase plays an important role.[7,8] Research has mainly investigated the effects of the cationic surfactants and the preparation process.[7–13] The results of these works showed that the cationic surfactants influence the structure and the properties of hybrid materials.

Montmorillonite (MMT) is a hydrated alumina–silicate clay composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The Na^+ or Ca^{2+} residing in the interlayers can be replaced by organic cations such as alkylammoium ions via an ion-exchange reaction to make the hydrophilic silicate lipophilic and to render it good dispersion in the organic polymer phase.

Since the dispersion of the clay is important in determining the subsequent hybrid materials preparation, it is essential to improve the interaction between the clay and the polymer matrix to produce a useful polymer composite. This work was done mainly to study the influence of the silcone coupling agent, methacyloxypropyltrimethoxysilane (MPTMS), on the structure and properties of a poly(methyl methacrylate) (PMMA)/MMT nanocomposite. The silicone coupling agent reacted with the hydrogen group on the clay surface to obtain surface-modified MMT. Then, organophilic clay was obtained via an ion-exchange reaction. The polymer/MMT nanocomposite was prepared by *in situ* bulk polymerization. The structure and properties of the composites were studied.

EXPERIMENTAL

Materials

Na^+–MMT was provided by the Zhejiang Huate Clay Co., Ltd. (China). It has an ion-exchange capacity of 100 mequiv/100 g. Methyl methacrylate (MMA) was distilled under a vacuum before use. MPTMS, 2,2'-azobisisobutyronitile (AIBN), and cetyltrimethylammonium bromide (CTAB) was used as received.

Modification of MMT

Ten grams of MMT was suspended in 200 mL of acetone, and 2 mL of MPTMS was dropped into the suspension. The mixture was stirred vigorously for 72 h at room temperature. Then, the suspension was filtered using a Busch filter and washed with acetone three times. The product was dried under a vacuum for 24 h at room temperature and crushed into a powder. The modified MMT was designated as M-MMT.
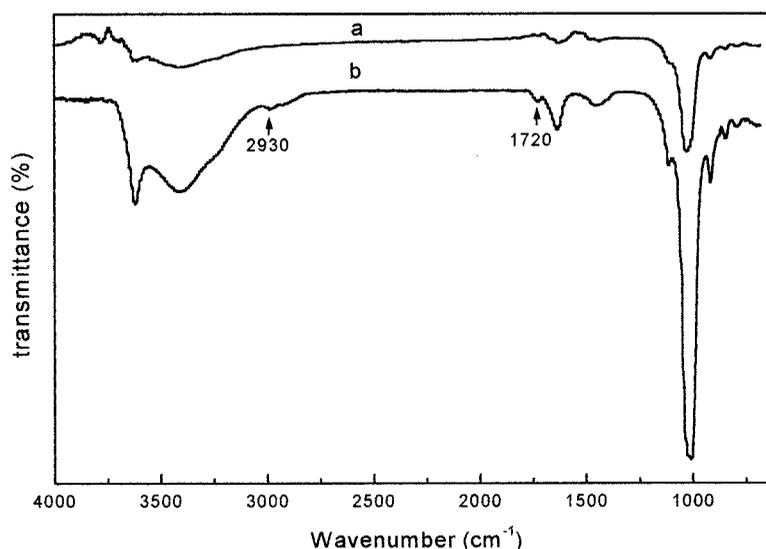
Figure 1 FTIR spectra of (a) MMT and (b) M-MMT.

Preparation of organophilic MMT

Organophilic MMT was prepared by an ion-exchange reaction. Ten grams of MMT (or M-MMT) was suspended in 1000 mL of distilled water at room temperature. CTAB, 4.0 g, was dissolved in 200 mL of hot distilled water and slowly poured into the MMT suspension. The suspension was stirred for 24 h at room temperature. The exchange clay was filtered and washed three times. The product was dried under a vacuum at room temperature for 24 h and crushed into a powder using a mortar and pestle. The organophilic MMT was designated as MMT–CTAB (or M-MMT–CTAB).

Preparation of PMMA/MMT nanocomposites

MMT, 1.05 g, was suspended in 20 g MMA. The mixture was stirred for 4 h. AIBN, 0.1 g (0.5 wt % of monomer), was added and stirred for 1 h. Then, the mixture was polymerized at 50°C for 24 h. The composite was postcured in an oven at 100°C.

Characterization and measurements

FTIR spectra were recorded on an AVATAR360 FTIR in the range of 4000–400 cm^{-1}. The KBr pellet method was used. X-ray diffraction (XRD) analysis was performed on a Rigaku D/max rB X-ray diffraction analyzer equipped with a rotating-anode generator system using CuKα ($\lambda = 1.54$ Å) radiation. The operating current was 120 mA and the voltage was 50 kV; the scanning rate was 1°/min. DSC was conducted on a DSC2910 modulated DSC (TA Instruments) from room temperature to 200°C at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a TGA-2950 thermogravimetric analyzer
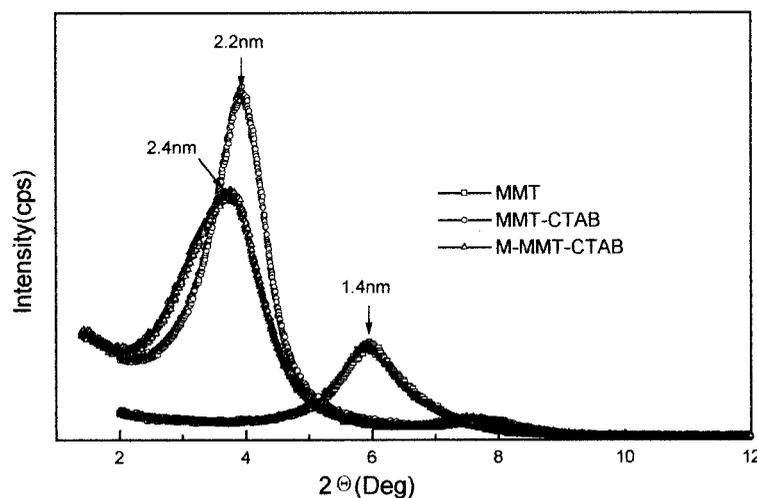

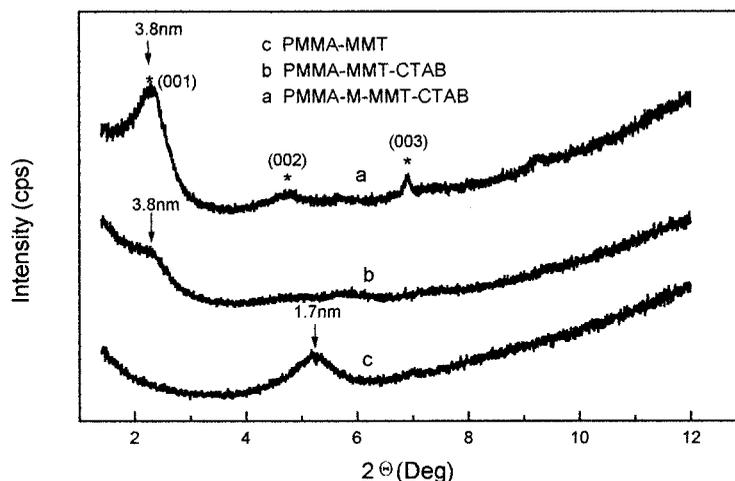**Figure 2** XRD patterns of MMT, MMT–CTAB, and M-MMT–CTAB.

Figure 3 XRD patterns of PMMA/clay nanocomposites (5 wt %) prepared with (a) M-MMT–CTAB, (b) MMT–CTAB, and (c) MMT.

(DuPont); the temperature range was room temperature to 600°C and the heating rate was 20°C/min.

RESULTS AND DISCUSSION

Structural characterization of M-MMT

There are hydroxy groups on the Si and Al atoms of the lamellar. The CH_3O— groups of the silicone coupling agent, MPMTS, can react with them at room temperature. MPMTS can be tethered on the surface of MMT. Figure 1 shows the FTIR spectra of MMT and M-MMT. Two new weak absorption peaks at 1720 and 2930 cm^{-1} can be seen. The two absorption peaks can be associated, respectively, with C=O stretching and C—H stretching. This means that MPMTS is attached on the surface of MMT.

The XRD spectra of MMT, MMT–CTAB, and M-MMT–CTAB show a slightly larger interlayer spacing

(d = 2.4 nm) of M-MMT–CTAB than that of MMT–CTAB (d = 2.2 nm) (Fig. 2). This phenomenon means that tethered MPMTS improves the CTAB penetratration into the interlayer region and the interlayer expansion of MMT.

Structural characterization of PMMA/clay nanocomposites

Figure 3 shows XRD patterns of PMMA/clay hybrids with 5 wt % of MMT. It is obvious that the polymer chain intercalates into MMT for all the samples. As shown in the figure, the interlayer spacing of PMMA–MMT (d = 1.7 nm) has only a 0.3-nm increase over that of virgin MMT (d = 1.4 nm). The hybrids of MMT–CTAB and M-MMT–CTAB all have 3.8-nm basal spacing, with a 1.6 and 1.4 nm increase over the corresponding organophilic MMT. However, for the
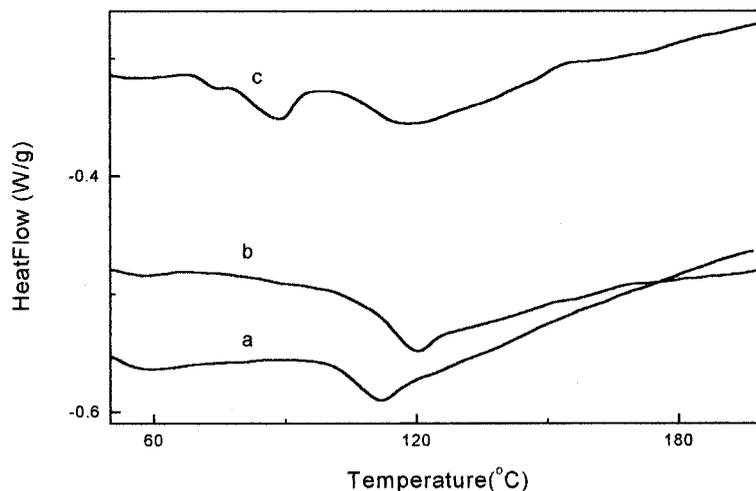

Figure 4 DSC thermograms of PMMA/clay nanocomposites (5 wt %) prepared with (a) M-MMT–CTAB, (b) MMT–CTAB, and (c) MMT.

TABLE I
Properties of PMMA/Clay Nanocomposites

Sample of nanocomposites	T_g(°C)	Onset temperature (°C)	T, for 20 wt % loss (°C)
Pure PMMA	100	240	284
MMT	111	245	306
MMT–CTAB	115	356	362
M-MMT–CTAB	106	342	348

PMMA–M-MMT–CTAB hybrid, higher-order peaks appear corresponding to $d_{(002)}$ and $d_{(003)}$, suggesting that the polymer chain intercalation does not damage the layer structure of the clay. In contrast, for the PMMA–MMT–CTAB hybrid, the absence of $d_{(002)}$ and $d_{(003)}$ and the small remnant shoulder at $2\theta = 2.4°$ ($d = 3.8$ nm) indicates that the layer structure is damaged and a highly disordered dispersion of the clay layer is obtained.

The MPMTS tethered on the surface of the clay could polymerize with MMA while polymerizing. The polymer attached on the surface prevents the layer structure from being damaged and the ordered structure is maintained compared with that of PMMA–MMT–CTAB.

Properties of PMMA/clay nanocomposites

Figure 4 shows DSC thermograms of nanocomposites prepared with different MMTs. It shows that the PMMA/clay nanocomposites have an elevated transition temperature (T_g) compared with that of pure PMMA. Table I shows the T_g value of these nanocom-

posites. It can be seen that the T_g of nanocomposites has a 6–15°C increase over that of pure PMMA. The T_g of PMMA–M-MMT–CTAB ($T_g = 106°C$) is lower than that of the other two nanocomposites ($T_g = 111$ and $115°C$, respectively). This may be associated with the dispersion of the clay layer. The more disordered dispersion of the clay layer causes the higher T_g increase. For nanocomposites prepared with M-MMT–CTAB, the layer structure of MMT is maintained. However, for the other two nanocomposites, the disordered structure is obtained.

The TGA analysis of these nanocomposites is shown in Figure 5. Evidently, the onset of thermal decomposition for the nanocomposites shifts to higher temperatures. The onset temperature of the nanocomposites prepared by M-MMT–CTAB and MMT–CTAB has a 100–120°C increase over that of pure PMMA and PMMA–MMT. The temperature for a 20 wt % loss of nanocomposites is much higher than that for pure PMMA. A summary of the DSC and TGA data is given in Table I.

The results of the DSC and TGA analyses show that the MPMTS tethered on the surface of the clay influences the properties of the hybrid materials. All these can be attributed to the dispersion of MMT in the polymer matrix. Breakage of the clay-ordered structure provides a great increase of interaction between the polymer matrix and the clay, resulting in an increase of the properties of the hybrids. The existence of MPMTS prevents the layer structure from being further delaminated and keeps the clay crystallites from being further damaged, which could decrease the function of the silicate layer as enhancement due to its high aspect ratio and surface area.
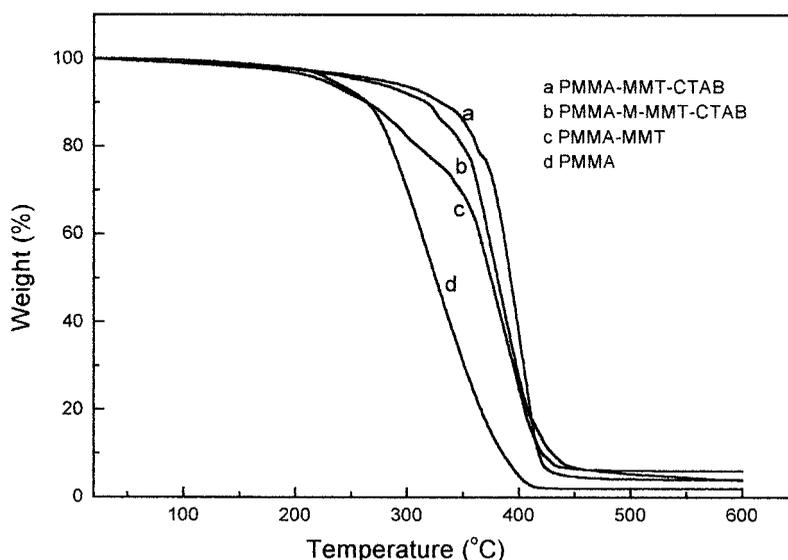

Figure 5 TGA curve of PMMA/clay nanocomposites (5 wt %) prepared by (a) M-MMT–CTAB, (b) MMT–CTAB, and (c) MMT.

CONCLUSIONS

The modification of MMT with the silicone coupling agent did not affect the interclation of the polymer chain, but influenced the dispersion of MMT in the polymer matrix. The smectic structure of the clay layer was maintained in nanocomposites prepared with modified organophilic MMT. DSC and TGA analyses showed great improvements in the thermal properties. There was a 6–15°C increase in the T_g and a 100–120°C increase in the T_d. However, the T_g and T_d of PMMA–M-MMT–CTAB was lower than that of PMMA–MMT–CTAB, but higher than that of pure PMMA.

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