A one-pot method to prepare transparent poly(methyl methacrylate)/montmorillonite nanocomposites using imidazolium-based ionic liquids

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Abstract

Poly(methyl methacrylate) (PMMA)/montmorillonite (MMT) nanocomposites were prepared by a new one-pot technique, where the hydrophilic Na-MMT layers were decorated with hydrophobic 1-dodecyl-3-methylimidazolium hexafluorophosphate (C12mimPF6) ionic liquid in situ during melt blending with PMMA and intercalation of polymer chains took place subsequently. The in situ modification and intercalation of Na-MMT were confirmed using X-ray diffraction and transmission electron microscopy. The combination of the compatible C12mimPF6 with PMMA and the good dispersion of MMT layers at the nanoscale rendered the resultant PMMA/MMT nanocomposites with improved optical transparency, thermal stability and mechanical properties.

INTRODUCTION

Polymer/layered silicate nanocomposites have attracted a great deal of attention due to the remarkable properties enhancement, including mechanical properties, thermal stability, flame retardancy and barrier properties. Such nanocomposites can be prepared by dispersing silicate layers in a polymeric matrix, using three main methods: in situ polymerization, solution blending and melt blending.

Montmorillonite (MMT) is one of the most widely employed layered silicates, because of its natural abundance together with high stiffness and swelling behavior. The most promising feature of MMT is that its interlayer spacing can be extensively expanded, which is necessary for the preparation of polymer/layered silicate nanocomposites. Nevertheless, the dispersion of MMT in polymer matrices is impeded by the incompatibility between the hydrophilic MMT surface and hydrophobic polymers. Thus the organic modification of MMT by ion-exchange reaction between pristine MMT and organic surfactant molecules is of great significance, which increases the interlayer spacing and the organophilicity of the MMT layers and consequently enhances their compatibility with organic polymers.

Conventionally, alkylammonium surfactants are widely used to prepare organophilic MMT using standard ion-exchange techniques. However, the MMT usually needs a long time (hours or even days) to be organically modified before it can be blended with polymers. Furthermore, alkylammonium-treated MMT has low thermal stability, resulting from the low decomposition temperature of the alkylammonium cations. By comparison, imidazolium cations are more thermally stable.

Alkylimidazolium-treated MMT has onset and maximum decomposition temperatures about 100 °C higher than those of the corresponding alkylammonium-treated MMT. Alkylimidazolium-based ionic liquids, which are organic salts with melting points below 100 °C, have been the focus of many reports on the organic modification of MMT. Alkylimidazolium-based ionic liquids are reported as potential functional additives for improving the material properties of polymers, because of their non-volatility, non-flammability, recyclability, thermal stability, unique solvating ability, adjustable hydrophilicity and high ionic conductivity. For example, 1-butyl-3-methylimidazolium hexafluorophosphate is found to be an effective plasticizer for poly(methyl methacrylate) to modulate the glass transition temperature (Tg) over a widened temperature range and improve the thermal stability of PMMA in comparison to traditional dioctylphthalate plasticizer.
In the study reported here, an ionic liquid (1-dodecyl-3-methylimidazolium hexafluorophosphate, C12 mimPF6) composed of an imidazolium cation with a long alkyl group and hexafluorophosphate anion was used as a hydrophobic modifier for MMT and a plasticizer for PMMA as well. Due to the unique compatibility of alkylimidazolium-based ionic liquids with MMT and PMMA, a new one-pot method to prepare polymer/MMT nanocomposites was proposed and experimentally verified. By this method, hydrophilic MMT could be organically modified with C12 mimPF6 and further intercalated with PMMA during melt blending, eliminating the time-consuming process of organic modification of MMT in an advance step. The intercalation and even exfoliation of MMT layers were confirmed using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, the high light transmittance of the nanocomposites obtained was validated using UV-visible spectroscopy, and the dynamic mechanical and thermal properties were characterized using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

PMMA was obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). Pristine sodium MMT (Na-MMT) with a cation exchange capacity (CEC) of 90 mmol (100 g)\(^{-1}\) was purchased from Qinghe Chemical Factory (Hebei, China). 1-Dodecyl-3-methylimidazolium bromide (C12 mimBr) and C12 mimPF6 were supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Organic-MMT, which had been organically modified using N,N-dimethyl-N,N-octadecylammonium chloride, designated AMMT, was supplied by Xi’an Changzhi Factory. All reagents were used as received.

Synthesis of nanocomposites

The nanocomposites were prepared using two methods: a one-pot melt method (OM) and a typical two-step melt intercalation (TM).\(^{16–20}\)

Preparation of nanocomposites by OM

Na-MMT was melt-blended with PMMA in the presence of C12 mimPF6, which has potential as a multifunctional additive for polymer materials, without the need for organic modification in advance. PMMA was blended with C12 mimPF6 and Na-MMT directly in a batch mixer (Haake RC90 Rheomix 600) at 200 °C. The rotator speed was 30 rpm for the initial 4 min, and then increased to 50 rpm for another 6 min. The samples were prepared with a C12 mimPF6 content of 2.5% and various Na-MMT contents of 0, 0.5, 1 and 2 wt%, which are designated as OM-IL2.5, OM-MMT0.5-IL2.5, OM-MMT1-IL2.5 and OM-MMT2-IL2.5, respectively. A nanocomposite with a C12 mimPF6 content of 5 wt% and Na-MMT content of 1 wt%, OM-MMT1-IL5, was also prepared.

Preparation of nanocomposites by TM

For comparison, Na-MMT was modified with C12 mimBr in water using a standard ion-exchange technique to synthesize organophilic MMT (C12 mim-MMT). An amount of 1.5 eq. of C12 mimBr with respect to the CEC value of Na-MMT was used. The mixture was refluxed under stirring for 6 h. Then the treated MMT was filtered and washed with distilled water until no Br\(^-\) was detected. It was dried in vacuum and then ground to a fine powder in an agate mortar. TM nanocomposites were prepared by melt-blending PMMA and C12 mim-MMT under the same conditions as for OM nanocomposites. Samples with C12 mim-MMT contents of 0.5, 1 and 2 wt% are designated as TM-CMMT0.5, TM-CMMT1 and TM-CMMT2, respectively.

RESULTS AND DISCUSSION

Microstructures of PMMA/MMT nanocomposites prepared by OM

In this study, the structure of nanocomposites and MMT at the nanometer scale was characterized using XRD patterns and TEM images, which can show directly the dispersion of MMT layers after intercalation of organic cations and polymer chains.

The XRD patterns of OM samples are shown in Fig. 1(a), and those of Na-MMT, C12 mim-MMT and TM samples are shown in Fig. 1(b) for comparison. Both OM-MMT2-IL2.5 and OM-MMT1-IL2.5 exhibit a narrow diffraction peak at 2θ = 2.8°, while Na-MMT shows a peak at 2θ = 9.0°. The interlayer spacing of MM has increased markedly from 0.98 nm in Na-MMT to 3.18 nm in OM samples, which is also larger than those of C12 mim-MMT (1.73 nm) and TM samples (2.74 nm). Accordingly, as demonstrated in Figs 2(a) and (b), the platelets in both OM samples consist of multilayers and exhibit intercalated microstructure. During the melt blending, both C12 mimPF6 molecules/C12 mim cations are suggested to diffuse into the galleries of Na-MMT. Consequently, the conversion of the hydrophilic surface of MMT layers to a hydrophobic surface and the subsequent intercalation of PMMA into the hydrophobic galleries take place in one pot to form orderly intercalated nanocomposites.
Some intercalated organic salts would take part in the ion-exchange reaction between Na-MMT and an ionic liquid, and facilitate the intercalation of Na-MMT. The ionic nature of the ionic liquid may result in strong attractive interaction with MMT layers, and facilitate the intercalation of Na-MMT (more than three times the CEC of Na-MMT). Therefore, the one-pot method proposed in this study is more effective than the standard two-step method to prepare nanocomposites from Na-MMT directly.

Moreover, the addition of C12mimPF6 in the preparation of OM-MMT2-IL2.5 and OM-MMT1-IL2.5 is in large excess over the amount needed to modify Na-MMT (more than three times the CEC of Na-MMT). The ionic nature of the ionic liquid may result in strong attractive interaction with MMT layers, and facilitate intercalation of C12mimPF6 molecules into the galleries of MMT. Some intercalated organic salts would take part in the ion-exchange reaction between Na+ and C12mim cations, while others may be adsorbed by the MMT layer via electrostatic interaction. Therefore, the one-pot method proposed in this study is more effective than the standard two-step method to prepare nanocomposites from Na-MMT directly.

The marked expansion of Na-MMT galleries in OM nanocomposites is also ascribable to the high compatibility of C12mimPF6 with PMMA. Figure 3 shows SEM images of the fractured surface of PMMA/MMT nanocomposites. As shown in Fig. 3, all TM nanocomposites display similar SEM images of the fractured surface, which indicates that MMT is nearly exfoliated and dispersed in the sample with interlayer spacing not less than 4.43 nm (according to 2θ = 2.1°). TEM images further validate the exfoliated structure of the nanocomposites, as evident from Fig. 2(c). This is probably because of the large amount of excess C12mimPF6 (up to 16 times the CEC) in OM-MMT0.5-IL2.5. A PMMA/MMT nanocomposite, OM-MMT1-IL5, was also prepared using the one-pot method, which has the same ratio of C12mimPF6 to Na-MMT as OM-MMT0.5-IL2.5 but greater Na-MMT content of 1 wt%. The dispersion of MMT layers in OM-MMT1-IL5 is consistent with that in OM-MMT0.5-IL2.5, as validated by the XRD pattern (Fig. 1(a)) and TEM image (Fig. 2(d)). This indicates that the microstructure of the nanocomposites obtained is determined primarily by the amount of C12mimPF6. Large excess of C12mimPF6 extensively expands the MMT layer spacing, and facilitates the further diffusion of PMMA to separate the layers due to the high compatibility of C12mimPF6 with the polymer matrix.

In the one-pot method, the hydrophobic Na-MMT is decorated with alkylimidazolium-based ionic liquid in situ during melt blending. It is more efficient and feasible in comparison with the time-consuming standard two-step method for the preparation of polymer nanocomposites with a prior ion-exchange procedure. Furthermore, the obtained hydrophobic galleries of MMT favor the intercalation of polymer chains to further enlarge the interlayer spacing. Therefore, better intercalation and even exfoliation of MMT can be obtained in OM nanocomposites, as shown in Fig. 1(a).

Microstructures of PMMA/MMT nanocomposites prepared by TM

The PMMA nanocomposites prepared by TM, i.e. Na-MMT was modified using the standard ion-exchange technique before it was blended with PMMA, were characterized as a comparison. As shown in Fig. 1(b), all TM nanocomposites display similar XRD patterns in the 2θ range between 2° and 10°. The diffraction peak shifts from 2θ = 5.1° corresponding to 1.73 nm for C12mim-MMT to 2θ = 3.2° corresponding to 2.74 nm after melt intercalation, indicating an enlarged interlayer spacing. The modification of Na-MMT renders the layer surface organophilic and improves the compatibility with polymer, which facilitates the further intercalation of polymer chains during melt blending. The diffusion of PMMA chains into C12mim-MMT galleries results in the formation of intercalated PMMA nanocomposites.

Physical and mechanical properties of PMMA/MMT nanocomposites prepared by OM

The dispersion of high-aspect-ratio MMT platelets in PMMA matrix at the nanoscale, which is confirmed by XRD patterns, would result in dramatic enhancements in physical and mechanical properties of the OM nanocomposites compared to neat PMMA.

Optical properties

Figure 4 shows digital photos of various samples in front of the logo of the Institute of Chemistry, Chinese Academy of Sciences.
Sciences. By visual inspection, the homogeneous OM samples have high optical transparency similar to neat PMMA, which is generally accepted as a transparent material. On the contrary, the PMMA/Na-MMT composite prepared by melt blending exhibits obvious aggregation of Na-MMT in the transparent polymer matrix. Therefore, the OM nanocomposites films were further characterized using UV-visible spectroscopy along with neat PMMA film as reference.

The transmittance values of neat PMMA and OM film samples at a wavelength of 800 nm were recorded and are given in Table 1. OM-IL2.5 film displays almost the same transmittance as the neat PMMA film, indicating the addition of C12mimPF6 does not decrease the optical transparency of PMMA matrix due to their good compatibility. With the addition of Na-MMT, the transmittance remains high for nanocomposite films up to 1 wt% of Na-MMT (OM-MMT0.5-IL2.5 and OM-MMT1-IL2.5). On increasing the Na-MMT content to 2 wt%, OM-MMT2-IL2.5 film still has a relatively high transmittance of 85.6 ± 0.6%. These results indicate the agglomeration only at the nanoscale formed from MMT layers and the good dispersion in the polymer matrix with the assistance of C12mimPF6. This further confirms the efficiency of the one-pot method for the preparation of polymer nanocomposites.

Dynamic mechanical properties
The thermomechanical properties of the OM samples were characterized using DMA with neat PMMA as comparison. The storage modulus ($G'$) as a function of temperature and $T_g$ were obtained during the characterization.

$G'$ of the samples is plotted for the temperature range from 30 to 165 °C in Fig. 5. $G'$ is related to the ability of a material to store mechanical energy during deformation. At temperatures below about 100 °C, all the samples have high modulus, which is observed to decrease slowly with increasing temperature. Above 110 °C, $G'$ decreases steeply with an increase of temperature,
Table 1: Properties of neat PMMA and one-pot samples

<table>
<thead>
<tr>
<th></th>
<th>Neat PMMA</th>
<th>OM-IL2.5</th>
<th>OM-MMT0.5-IL2.5</th>
<th>OM-MMT1-IL2.5</th>
<th>OM-MMT2-IL2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmittance (%)</td>
<td>89.7 ± 0.9</td>
<td>89.1 ± 0.5</td>
<td>90.0 ± 0.3</td>
<td>89.8 ± 0.5</td>
<td>85.6 ± 0.6</td>
</tr>
<tr>
<td>( T_g ) (°C)</td>
<td>122.4</td>
<td>117.7</td>
<td>118.1</td>
<td>120.5</td>
<td>122.7</td>
</tr>
<tr>
<td>( T_d ) (°C)</td>
<td>341.2</td>
<td>346.3</td>
<td>346.7</td>
<td>348.1</td>
<td>349.1</td>
</tr>
</tbody>
</table>

\(^a\) Transmittance at 800 nm obtained from UV-visible spectra.
\(^b\) X ± Y: X indicates the mean of the transmittance values of five sample points, while Y is the variance.

Table 1 shows \( T_g \) obtained from the peak temperature of loss angle tangent (\( \tan \delta \)) for neat PMMA and OM samples. It is observed that the \( \tan \delta \) peak shifts to lower temperatures with addition of \( C_{12}\text{mimPF}_6 \), and then to higher temperatures with increasing loading of Na-MMT, compared to neat PMMA. When the Na-MMT content is 2 wt\%, \( T_g \) of OM-MMT2-IL2.5 is equal to that of neat PMMA. The excess \( C_{12}\text{mimPF}_6 \) is responsible for the decrease of \( T_g \) for the OM samples. Therefore, these results are consistent with those for \( G' \), indicating that the well-dispersed MMT layers and excess compatible \( C_{12}\text{mimPF}_6 \) have opposite effects on the mobility of polymer chains. Moreover, these effects also similarly influence the mechanical properties, e.g., tensile strength and impact strength, of these nanocomposites (data not shown here).

Thermal stability

In this study, an alkylimidazolium-based ionic liquid was used as the organic modifier of Na-MMT mainly due to the better thermal stability of imidazolium cations than alkylammonium ones. In order to study the interaction between \( C_{12}\text{mim} \) cations and MMT layers, TGA analysis was applied. Figure 6 shows the TGA and derivative thermogravimetry (DTG) curves of \( C_{12}\text{mim-MMT} \) along with pristine Na-MMT and two ionic liquids in nitrogen atmosphere. The mass loss of Na-MMT occurs from 500 to 750 °C and has a maximum rate at about 681 °C, which is due to the dehydroxylation of the aluminosilicate lattice. However, \( C_{12}\text{mim-MMT} \) exhibits two discrete decomposition events between 250 and 500 °C, indicating the degradation of organic components, while the organic modifier \( C_{12}\text{mimBr} \) used for preparing \( C_{12}\text{mim-MMT} \) displays single-step decomposition between 200 and 350 °C with the DTG peak at about 299 °C (Fig. 6(b)). Consequently, both decomposition events for \( C_{12}\text{mim-MMT} \) have higher temperatures related to the maximum rate of mass loss than that of \( C_{12}\text{mimBr} \). These results indicate that the presence of MMT layers with nanosized spacing influences the degradation process, products and kinetics of organic component therein. These two events might be assigned to two molecular environments of \( C_{12}\text{mimBr}/C_{12}\text{mim cations in MMT layers. The mass loss at 371 °C can be attributed to the } C_{12}\text{mimBr molecules physically adsorbed onto the surface of MMT layers, while that}

Figure 4. Digital photos of (a) neat PMMA, (b) OM-IL2.5, (c) OM-MMT1-IL2.5 and (d) OM-MMT2-IL2.5 samples in front of ICCAS logo.

Figure 5. Storage modulus versus temperature for neat PMMA and one-pot samples.

indicating the samples lose their stiffness quickly due to the glassy to rubbery state transition. OM-IL2.5 exhibits a smaller \( G' \) relative to neat PMMA in the whole temperature range studied because of the plasticization effect of \( C_{12}\text{mimPF}_6 \), which is consistent with previous studies. In contrast, \( G' \) increases with further addition of Na-MMT up to 2 wt%, resulting from the high stiffness of the inorganic filler. For example, the storage modulus of OM samples at 60 °C increases from 2.45 GPa for OM-IL2.5, to 2.55 GPa for OM-MMT0.5-IL2.5, 2.75 GPa for OM-MMT1-IL2.5 and 2.86 GPa for OM-MMT2-IL2.5. In the low-temperature region, the loading of 0.5 wt% MMT nearly offsets the loss of storage modulus by 2.5 wt% of \( C_{12}\text{mimPF}_6 \), and OM-MMT1-IL2.5 exhibits higher \( G' \) than neat PMMA. However, in the high-temperatures region, \( G' \) of all OM nanocomposites is smaller than that of neat PMMA. This is probably attributable to the quickly decreasing modulus of polymer matrix in the presence of excess \( C_{12}\text{mimPF}_6 \), which would be in the liquid state at these temperatures.
A new one-pot method was proposed in this study to prepare transparent PMMA/MMT nanocomposites. Using this method, the hydrophilic Na-MMT layers were decorated with hydrophobic C12mimPF6 ionic liquid in situ during 10 min melt blending with PMMA, where the intercalation of polymer chains took place subsequently. Accordingly, the method has the distinct advantage of greater efficiency than the time-consuming standard ion-exchange procedure for Na-MMT modification. As a potential additive for polymer materials, excess C12mimPF6 remained in the nanocomposites, further leading to larger interlayer spacing, as revealed by XRD analysis. Moreover, the presence of well-dispersed MMT layers and compatible C12mimPF6 in PMMA endows the obtained PMMA/MMT nanocomposites with high optical transparency and thermal stability. The bulk stiffness and chain mobility of the nanocomposites are determined by the combination of the plasticization effect from C12mimPF6 and the reinforcement effect from MMT layers at the nanoscale.

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**REFERENCES**


