Effect of organically modified montmorillonite on thermal degradation mechanism of polycarbonate nanocomposites

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Abstract

By studying previous reported papers, there were contradictory results about the effect of clay on thermal stability of polycarbonate (PC). For ascertainment of the actual role of clay, PC nanocomposites were prepared by direct melt-mixing PC with hexadecyl trimethyl ammonium chloride modified montmorillonite (OMT). The results of XRD, TEM and HREM experiments present the formation of uniformly intercalated structure. TGA shows the onset decomposition temperature of PC/OMT nanocomposites is earlier 65 °C than pure PC. The mechanism of PC thermal decomposition effected by OMT was discussed in detail. It reveals that OMT can catalyze thermal degradation of PC chains and decrease thermal stability of the nanocomposites.

Keywords: PC; Nanocomposites; TGA; Thermal stability; Thermal degradation mechanism

1. Introduction

Bisphenol A polycarbonate (PC) is a commercially important amorphous engineering thermoplastic with many valuable properties including high impact strength over a wide temperature range, heat resistance, dimensional stability, and optical transparency. While PC has very attractive thermal-mechanical properties, improvement in impact resistance, tensile properties and fire retardancy would expand potential applications for this material. So, it is practical to research ways to improve upon its already inherent qualities.

Polymer nanocomposites, especially polymer/clay nanocomposites, have been an important and feasible approach. Since a nylon-6/clay hybrid material reported by the Japanese industrial research group \cite{1} and melt-mixing method without the use of organic solvents used by Giannelis et al. \cite{2}, polymer clay nanocomposites have attracted a remarkably strong attention of academic and industrial researchers. From fundamental science viewpoint, the two kinds of nanocomposite structure, intercalated and exfoliated morphologies, respectively offer well-defined model systems with macroscopic quantities of 1-2 nm thin confined polymer films and polymer brushes \cite{3}. From an industrial viewpoint, the dispersion of these ultra-thin (1 nm) ultra-high surface-area fillers in polymers concurrently improves many properties of the materials, namely mechanical, thermal, barrier, and solvent resistance, and also provides a flame retardant character \cite{4}.

Recently, PC/clay nanocomposites have been prepared by in-situ intercalative polymerization \cite{5-7} and polymer melt intercalation \cite{8-14} using alkyl ammonium or phosphonium modified clay. This ambiguity may seem paradoxical about the effect of clay on thermal stability of PC nanocomposites. Some papers indicated the decrease of thermal stability of PC nanocomposites \cite{5, 8, 9, 11, 14}, while another studies showed the improvement of decomposition temperature of PC nanocomposites \cite{6, 10, 12, 13}. Generally, the clay has two opponent effects in the thermal stability of the polymer/clay

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nanocomposites. The barrier effect should improve the thermal stability; the promoter effect would encourage the degradation process and the other is the catalysis effect towards the degradation of the polymer matrix which would decrease the thermal stability [15, 16]. But the comprehensive effect of clay is uncertain and depends on the composition, structure, thermal environment and so on.

For ascertainment of the actual role of clay, PC nanocomposites were prepared by melt-mixing PC with organically modified montmorillonite (OMT) in this study. Morphology and thermal property of PC/OMT nanocomposites were respectively analyzed by XRD, TEM, HREM and TGA. And the thermal degradation mechanism of PC/OMT nanocomposites was discussed in detail.

2. Experimental

2.1. Materials

The PC used in this study was manufactured from Teijin chemicals LTD., Japan (K-1300, density=1.20). The original purified sodium montmorillonite (MMT, with a cation exchange capacity of 96 meq/100g) and hexadecyl trimethyl ammonium chloride modified montmorillonite, OMT, were kindly provided by Keyan Company, China.

2.2. The preparation of PC/OMT nanocomposites

The clay and the PC pellets were dried under vacuum at 80 °C for at least 10 h before use. PC with 5 wt% clay was melt-mixed 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.

2.3. Characterization

The dispersibility of the silicate layers in the PC was evaluated using X-ray diffractometry (XRD), high-resolution electron microscopy (HREM) and bright field transmission electron microscopy (TEM). Films (1mm) of the nanocomposites 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°. HREM and 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. HREM images were obtained by JEOL 2010 with an acceleration voltage of 200 kV. TEM images were obtained on a JEOL JEM-100SX microscope with an acceleration voltage of 100 kV. Thermogravimetric analyses (TGA) were carried out from room temperature to 700 °C using a Netzch STA-409c thermal analyzer under nitrogen flow at the rate of 10 °C/min.

3. Results

3.1. Structure of PC/OMT nanocomposites

Figure 1 shows the XRD patterns of MMT, OMT and PC/OMT nanocomposites containing 5 wt% of OMT. The peaks correspond to the (001) plane reflections of the clays. The average basal spacing of MMT increases from 1.4 nm to 2.4 nm on organic modification, when the original MMT was modified by hexadecyl trimethyl ammonium chloride (C16). This increased spacing suggests the molecules of C16 intercalate into the gallery of MMT. The XRD pattern of PC/OMT nanocomposites presents that the spacing of the silicate layers increases from 2.4 to 2.8 nm and remains the second diffraction peak, indicating the formation of the intercalated morphology. But PC hybrids with 5 wt% of MMT exhibits only a weak peak corresponding to the same interlayer distance of 1.4 nm as that of pristine MMT, which indicates that PC cannot intercalate into the gallery of montmorillonite without organic modification.

To further confirm the dispersion of OMT in the PC matrix, electron microscopic measurements are required. The TEM and HREM micrographs are respectively presented in Figs. 2 and 3. The TEM image of PC/OMT nanocomposites at low magnification (Fig. 2) shows uniform distribution of the silicate layers in the PC matrix, suggesting great interaction between the silicate particles and the PC matrix. From Fig. 3 of HREM image, the intercalated structures of PC/OMT nanocomposites are confirmed by a significant number of tactoids with interlayer spacing about 3nm observed, which is consistent with the XRD result.
3.2. Thermal property of PC/OMT nanocomposites

The effect of OMT presence on the thermal stability of PC was analyzed by means of thermogravimetric analysis (TGA) in inert conditions. The TG curves of OMT, pure PC and PC/OMT nanocomposites are shown in Fig. 4. The onset decomposition temperature ($T_{\text{onset}}$, defined as the temperature at 5\% weight loss), the 50\% weight loss temperature ($T_{50\%}$) and char residue at 700 °C are listed in Table 1.
Fig. 4. TG curves for OMT, PC and PC/OMT nanocomposites.

Table 1. TGA Results for the Thermal Degradation of PC/OMT nanocomposites and pure PC

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{50%}$ (°C)</th>
<th>Charred residue at 700 °C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PC</td>
<td>487</td>
<td>520</td>
<td>26.7</td>
</tr>
<tr>
<td>PC/OMT</td>
<td>422</td>
<td>521</td>
<td>27.5*</td>
</tr>
</tbody>
</table>

*The char for organic modified montmorillonite at 700 °C has already been subtracted.

From TG curve of OMT, it revealed that free (absorbed) water residing between montmorillonite crystallites lose before 100 °C, and then interlayer water residing between the aluminosilicate layers and organic modifier evolve between 200-500 °C as the previous research [17]. Fig. 4 and Table 1 both indicated the great difference of thermal decomposition temperature between pure PC and PC/OMT nanocomposites. Although $T_{50\%}$ and charred residue at 700 °C are higher, $T_{\text{onset}}$ of PC/OMT nanocomposites is smaller 65 °C than pure PC. It showed that OMT catalyze degradation of PC chains and decrease thermal stability of PC/OMT nanocomposites. So polymer-layered silicate nanocomposites cannot at all improve thermal property, and it correlates with the composition, structure and mechanism of degradation [15].

4. Mechanism of thermal degradation of PC/OMT nanocomposites

There exits some inorganic hydrated cations in the aluminosilicate interlayer of OMT because the sodium gallery cations of montmorillonite cannot entirely be exchanged during organic modification by alkyl ammonium salts and some inorganic hydrated cations e.g. Al$^{3+}$ or Mg$^{2+}$ exist in the octahedral structure of montmorillonite which can be not substituted by ionic exchange [17]. So interlayer water residing between the aluminosilicate sheets gradually evolve between 200-500 °C. Interlayer water and hydroxyl group of the aluminosilicate sheets in OMT can catalyze thermal decomposition of PC by transesterification reaction as Scheme a. As shown by Scheme b, the surfactant in OMT meanwhile follows a Hoffmann elimination reaction approximately at 200 °C [14, 17, 18]. It results that $\alpha$-hexadecene and trimethyl amine evolve and Brønsted acid remains between the aluminosilicate galleries in OMT. The presence of Brønsted acid may further catalyze bisphenol A as main pyrolysis product of PC chains to generate phenol and 4-isopropenyl phenol (Scheme c and Scheme d). It is noteworthy that puny change of pyrolysis environment and physical property of PC macromolecule chain can evidently affect mechanism of thermal degradation of PC. During thermal decomposition of PC/OMT nanocomposites, clay layers are well dispersed and can impede the release of pyrolysis products with small molecule like phenol. If these small molecule products cannot evolve as quickly as possible, enrichment of phenol acting as Brønsted acid may result that interruption of chains plays dominant role while cross-link of chains is on subordinate status in the process of thermal degradation of PC macromolecule. After 500 °C, interlayer water of OMT entirely evolved and the TG curves of pure PC and PC/OMT nanocomposites almost coincided. With increase of thermal temperature, the barrier effect of OMT which should improve the thermal stability becomes obvious and promotes more charred residue at 700 °C of PC/OMT nanocomposites than pure PC.
(a) thermal decomposition of PC catalyzed by interlayer water or hydroxyl group of aluminosilicate sheets in OMT

(b) Hoffmann elimination reaction of alkyl ammonium cations in OMT

(c) bisphenol A as main pyrolysis product of PC catalyzed by Brønsted acid

(d) elimination reaction of Brønsted acid

Fig. 5. Scheme of thermal degradation of PC/OMT nanocomposites.
5. Conclusions

PC/OMT nanocomposites were prepared by direct melt intercalation with mixing PC and hexadecyl trimethyl ammonium chloride modified montmorillonite. XRD, TEM, HREM, and TGA experiments were respectively carried out to characterize the morphology and thermal properties of the nanocomposites. The results show the onset decomposition temperature of the formed intercalated-type nanocomposites is earlier 65 °C than pure PC. It was attributed that interlayer water or hydroxyl group of the aluminosilicate sheets or Brønsted acid as pyrolysis product of alkyl ammonium in OMT catalyzed thermal degradation of PC chains or bisphenol A.

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