Preparation and Characterization of Polyethylene Terephthalate/Montmorillonite Nanocomposites from Oligomerically Modified Montmorillonite

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Abstract. In this work, sodium montmorillonite was modified by a series of oligomeric surfactant (COPS-B, COPS-O and PBD). Such thermally stable oligomerically modified montmorillonites were further melt-compounded with polyethylene terephthalate (PET) at high temperature and three kinds of nanocomposites (PET/COPS-B-MMT, PET/COPS-O-MMT and PET/PBD-MMT) were obtained. The influence of structure and content of the oligomerically modified montmorillonites on the morphology and properties of the nanocomposites were evaluated. The results showed that the nanocomposites of PET/MMT had higher crystallization rate than pristine PET and the crystallization rate increased with the increase of MMT content.

Keywords: Nanocomposites, Polyethylene terephthalate, Montmorillonite, Oligomeric surfactant

1. Introduction

Polymer/clay nanocomposites have been demonstrated to possess significantly improved physical properties[1-5] and other enhanced properties including thermal[6,7] and flammability[8,9] over the virgin polymer. Polymer/clay nanocomposites can be obtained by direct polymer melt intercalation, which is the most industrially valuable method because of its environmentally benign character, its versatility, and its compatibility with current polymer-processing techniques[10,11]. PET is a semicrystalline polymer possessing excellent chemical resistance, thermal stability, melt mobility, and spinnability, but its uses are limited by its long crystallization time and poor impact strength [12-14]. With the addition of clay into pure PET, reduced gas permeability, enhanced thermal properties and shorter crystallization time are observed [15,16].

For the processing of PET composites, the high temperature, which is required for melt intercalation, generally induces decomposition of alkyl ammonium cations in the organic-modified montmorillonites [17]. Therefore high thermal stability of organo-clays is needed for the good dispersion of clay in the matrix polymer. To improve the thermal stability of organo-clays, the polymeric or oligomeric system is potentially a good choice for the organic modification of clay [18-21].

In this paper, we prepared organo-clays from a series of oligomeric surfactant. Furthermore, the obtained organo-clays were melt-compounded with PET to prepare PET/MMT nanocomposites.

2. Experimental

2.1. Materials

Sodium montmorillonite was prepared from raw mineral (purchased from Bentonite Company of Xinhe County in Inner Mongolia) by a method developed in our laboratory. The captions exchange capacity (CEC) of the sodium montmorillonite was 100 mmol/100 g. N,N-dimethyloctodecylamine, N,N-dimethylbenzylamine and 4-vinylbenzyl chloride were acquired from Aldrich Chemical Co. Styrene

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and benzoyl peroxide (BPO) were provided by Beijing Chemical Reagent Co. Polybutadiene （Mn=2000）was purchased from Aldrich Chemical Company. The PET and PBT were purchased from Shenzhen Yatai Company (PET4010N, PBT3010N).

2.2. Synthesis of Oligomeric Surfactant

The structure of oligomeric surfactants (PBD, COPS-B and COPS-O) was shown in Scheme 1. Polybutadiene surfactant (PBD) was prepared by grafting copolymerization of vinylbenzyl chloride onto polybutadiene initiated by BPO and then reacted with N,N-dimethylbenzylamine[18]. The oligomeric surfactant containing benzyl (COPS-B) and Octadecyl-based oligomeric surfactant (COPS-O) were prepared on the basis of reported method[21].
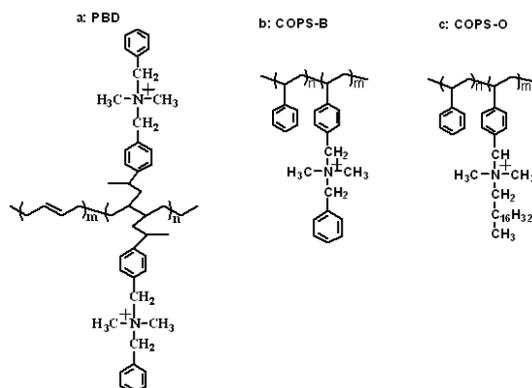
Scheme 1. Structure of the oligomeric surfactant used to treat sodium montmorillonite

2.3. Preparation of Oligomerically Modified Montmorillonite

The oligomerically modified montmorillonites were prepared by a cation-exchange reaction of Na^+ and oligomeric surfactant (PBD, COPS-B and COPS-O). The oligomerically modified montmorillonites were termed PBD-MMT, COPS-B-MMT and COPS-O-MMT.

2.4. Preparation of Polyester/MMT Nanocomposites

The PET/MMT nanocomposites were prepared by melt blending by twin screw extruder (SHJ-20, L/D=32, Φ=21.7). In order to obtain the same thermomechanical history, PET matrix were subjected to the same process.

2.5. Characterization

The range in gallery distance of the clay was monitored on a DB-ADVANCE X-ray diffractometer. Composite samples were melted and pressed to thin plates with a dimension of 10×10×1 mm.

Dispersibility of the silicate layers in the composites was evaluated by transmission electron microscopy (TEM). Samples were ultramicrotomed with a glass knife on a LKB-Ⅴ Ultratome at the temperature of -80～-90℃ to give about 70 nm thickness sections. The sections were transferred from the knife-edge to 400 hexagonal mesh Cu grids.

The crystallization temperatures of pure polymers and their composites were determined by using a differential scanning calorimeter (Perkin-Elemer-pyris1 DSC).

3. Results and Discussion

In this work, a series of oligomeric surfactant were used to treat sodium montmorillonite via standard ion-exchange methods to give oligomerically modified montmorillonites, which were used to prepare PET/MMT nanocomposites by melt processing using a twin screw extruder. Three kinds of composites including PET/PBD-MMT, PET/COPS-B-MMT and PET/COPS-O-MMT were prepared.

3.1. Morphology of the Organo-clays

The average basal spacing of clay (d_{001}) was calculated from the position of the main diffraction peaks in XRD. Figure 1 showed the XRD spectra of PBD-MMT, COPS-B-MMT and COPS-O-MMT. The corresponding spectrum of the Na-MMT was also given for comparison. No diffraction peak was observed

for COPS-B-MMT and COPS-O-MMT at 2θ between 2° and 10°, which resulted from $d_{001} > 5.3$ nm. The XRD diffraction peak of PBD-MMT was observed at about 5.8^{o}, which corresponded to the basal spacing of 1.56 nm. The XRD data showed that the oligomeric surfactants were well intercalated between the clay layers, leading to greater interlayer spacing.
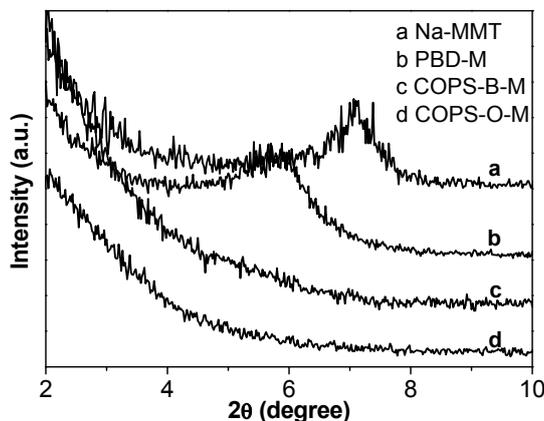

Fig. 1: XRD patterns of Na-MMT, PBD-MMT, COPS-B-MMT and COPS-O-MMT

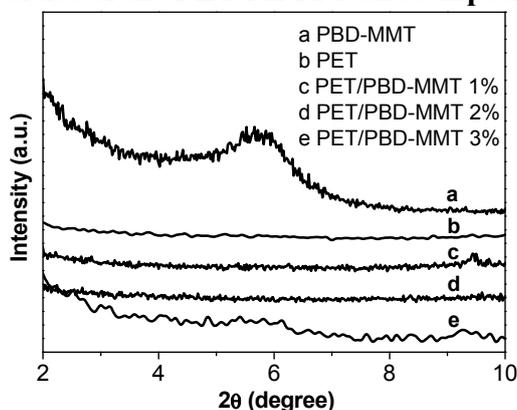## 3.2. Morphology and Properties of the PET/MMT Nanocomposites

Fig. 2: XRD patterns of PET/PBD-MMT

Figure 2 showed the XRD patterns of PET/PBD-MMT composites containing 1 wt%, 2 wt% and 3 wt% of clay. The characteristic (001) diffraction peak of PET/PBD-MMT was not detected in the composites with 1wt% and 2 wt% clay loading, which indicated that the diffraction peak of the composites was lower than 2° and corresponding to $d_{001} > 5.3$ nm. The increased d spacing suggested that PET chains intercalated into the gallery of PBD-MMT. When the content of clay in the composites increased to 3 wt%, a weak peak appeared at about 5.8^{o}, which corresponded to the (001) plane reflections of PBD-MMT. The results suggested that the amount of the unintercalated PBD-MMT increased with the increase of clay content.

No diffraction peak was observed for the PET/COPS-B-MMT and PET/COPS-O-MMT nanocomposites with different clay loading at 2θ between 2° and 10°, i.e., the d spacing of clay was so large enough that it is outside the XRD detection limit (2θ below 2°), and might permit the delamination of the clay, or the formation of an intercalated structure. Thus, a mixed morphology, including immiscible, intercalated and delaminated MMT structure, was probably obtained in the nanocomposites.

Transmission electron microscopy provides direct observation of morphology and dispersibility. TEM images of PET/PBD-MMT composite containing 2 wt% of clay were shown in figure 3. Low magnification TEM (figure 3 a) showed poor dispersion characterized by relatively large and well-separated particles in the micron range. At higher magnification (figures 3 b and c) the presence of expanded layers within the tactoids was apparent. The d spacing of clay was about 10 nm in the composite, which indicated that PET intercalated into the clay gallery space.
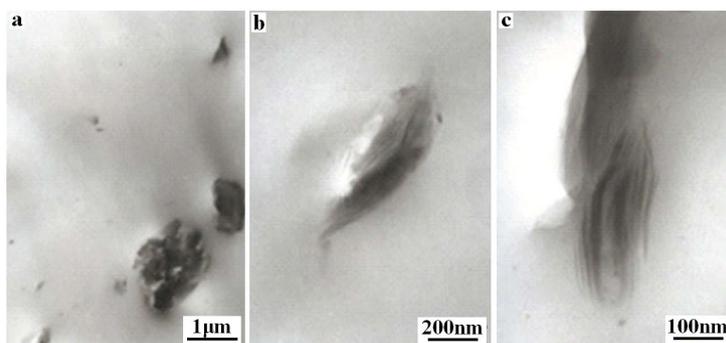
Fig. 3: TEM images of PET/PBD-MMT with 2 wt% clay loading

Figure 4 showed the TEM micrographs of PET/COPS-B-MMT and PET/COPS-O-MMT nanocomposites. The clay tactoids was well distributed and the mean value of the particle size was about 0.1 µm as shown in figures 4 a and c. The high-magnification TEM images of nanocomposites revealed that some individual clay layers were in registry with other clay layers (with interlayer spacing larger than 15 nm) while others did not show this registry as indicated in figures 4 b and d. This indicated that clay layers are partially intercalated and partially exfoliated in PET matrix, which was in agreement with the results of XRD.
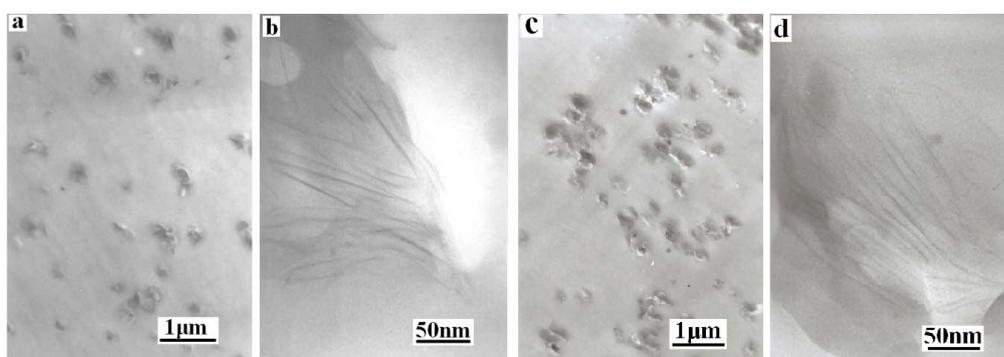

Fig. 4: TEM micrographs of PET/MMT with 2 wt% clay loading (a and b PET/COPS-B-MMT; c and d PET/COPS-O-MMT)

3.3. Crystallization Behavior of Polyester/MMT Nanocomposites

Table 1: DSC results of the polyester/MMT composites

Samples	T_{mc} (°C)	T_{cc} (°C)	T_m (°C)	$\Delta T = T_m - T_{mc}$ (°C)
PET	201	130	262	61
PET/COPS-B-MMT 1%	204	125	258	54
PET/COPS-B-MMT 2%	214	125	260	46
PET/COPS-B-MMT 3%	211	124	261	50
PET/COPS-O-MMT 1%	212	125	260	48
PET/COPS-O-MMT 2%	212	125	260	48
PET/COPS-O-MMT 3%	214	120	260	46
PET/PBD-MMT 1%	210	-	-	-
PET/PBD-MMT 2%	211	-	-	-

The crystallization behavior of PET/MMT nanocomposites was investigated by DSC. The PET/MMT nanocomposites were heated to melting temperatures for a period of 5 min to normalize the thermal history, and then were cooled at a rate of 10 °C /min. Melting crystallization temperature (T_{mc}) and its half peak width were two parameters that can characterize the crystallization rate. For the non-isothermal crystallization, the composites with high crystallization rate possessed high T_{mc} and narrow half peak width[22]. T_{mc} of the composites was obtained from DSC curves of cooling and the values of cooling crystallization temperature (T_{cc}) and melting temperature (T_m) were achieved from DSC. The DSC results for all nanocomposites were summarized in Table 1. The results showed that as compared with pure PET, PET/MMT composites exhibited a little lower melting temperature (T_m), lower cool crystallization temperature (T_{cc}), higher melting crystallization temperature (T_{mc}) and lower super cooling degree ($\triangle T$).

Hence, the PET/MMT nanocomposites had higher crystallization rate than pristine PET. Crystallization rate of PET/MMT nanocomposites increased with the increase of MMT content. One reason of crystallization rate enhancement was that MMT can act as an effective heterogeneous nucleating agent.

4. Conclusion

Three kinds of oligomeric surfactant (COPS-B, COPS-O and PBD) were used to modify clay. The d spacing of COPS-B-MMT and COPS-O-MMT was larger than 5.3 nm. The basal spacing of MMT increased from 1.22 nm to 1.56 nm after PBD modification. The obtained organo-clays were melt-compounded with PET to prepare PET/MMT nanocomposites. XRD, TEM and DSC experiments were carried out to characterize the morphology and properties of the nanocomposites. The results of XRD and TEM showed that PET/PBD-MMT system had intercalated structure. PET/COPS-B-MMT and PET/COPS-O-MMT nanocomposites had nanocomposites had partially exfoliated and partially intercalated structures. The results of DSC measurements indicated that crystallization rate of the PET increased with the adding of organo-clay, which was attributed to the nucleating effect of the clay particles.

5. Acknowledgements

6. References

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