

SYNTHESIS AND PROPERTIES OF POLYSTYRENE/LAPONITE NANOCOMPOSITES

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Abstract Exfoliated polystyrene (PS)/laponite nanocomposites were prepared successfully. The characteristic d_{001} diffraction peak of organo-laponite disappeared in the XRD patterns of nanocomposites, indicating that the laponite layers were exfoliated and the ordered crystal structure of laponite was destroyed because of the styrene polymerization. TEM observations showed that the exfoliated laponite primary particles were dispersed randomly in the PS matrix with lateral dimensions from 1 nm to 10 nm. SEM results showed that the PS/laponite nanocomposite particles were almost monodispersed spheres with the size of about 120 nm. Because of the interaction between PS and laponite nanolayers, the nanocomposites exhibited higher thermal stability and glass transition temperature when compared to pure PS.

Keywords Polystyrene (PS), Laponite, Nanocomposites

INTRODUCTION

During the past few years, polymer/clay nanocomposites (PCN) have attracted considerable interest because of the dramatic enhancements in physical, thermal, and mechanical properties of polymer-based materials with a relatively low amount of clay. Much effort has also been devoted to polystyrene (PS)/clay nanocomposites^[1–15]. However, the used clay minerals are mainly montmorillonite, and polystyrene/laponite nanocomposites have been reported rarely^[16]. Laponite, a totally synthetic hectorite clay, has a layered structure which is similar to that of montmorillonite. This layered hydrous magnesium silicate has been widely used in many different fields, such as drilling fluids, batteries, cosmetics and paints, because of its high degree of structural regularity and low levels of impurities^[17–20]. Sodium ions between the negatively charged silicate layers are readily exchanged for other ions (cation exchange capacity = 0.8 meq/g)^[21], which make it possible for polymer molecules to intercalate into the interlayer regions of laponite.

Polymer/clay composites are generally divided into three types: conventional composites, intercalated nanocomposites and exfoliated nanocomposites^[22]. Only the latter configuration is of particular interest because it maximizes the polymer-clay interactions, making the entire surface of the layers available for the polymer. This should lead to dramatic changes in mechanical and physical properties of the composites. Nevertheless, preparation of exfoliated PCN is relatively difficult, due to the strong electrostatic attraction between the clay layers and the intergallery cations, and few studies on exfoliated PS/clay nanocomposites have been reported^[7,10].

In this paper, we successfully prepared exfoliated PS/laponite nanocomposites. The structure, morphology, and thermal properties were studied in detail.

EXPERIMENTAL

Materials

Laponite RD was kindly provided by Rockwood Additives Limited. Bulk density 1000 kg/m³, surface area (BET)

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Received May 21, 2003; Revised October 13, 2003; Accepted October 20, 2003

370 m²/g, pH (2% suspension) 9.8, chemical composition (dry basis): SiO₂ 59.5%, MgO 27.5%, Li₂O 0.8%, Na₂O 2.8%, loss on ignition 8.2%; styrene was used as received from Shanghai Chemical Company. All the chemicals used were analytical reagent (AR) grade.

Synthesis of PS/Laponite Nanocomposites

Laponite was first modified to organo-laponite by cetyltrimethylammonium bromide (CTAB), and this process was according to a published method^[13]. The preparation procedure of the PS/laponite nanocomposites was described as follows. A desired amount of organo-laponite was dispersed in styrene, and an aqueous solution of ammonium persulfate and sodium dodecyl sulphate were added to form a stable water base emulsion. Then, the styrene was polymerized at 80°C for 3 h in the presence of N₂. Finally, the product was washed several times by deionized water and dried in an oven at 80°C, the PS/laponite nanocomposites were then obtained.

Characterization

X-ray diffraction (XRD) patterns were recorded by monitoring the diffraction angle (2θ) from 1.5° to 40° on a D/max- γ B X-ray diffractometer. The diffractometer was equipped with a CuK α radiation source operated at 40 kV and 120 mA, and the scanning speed was 2 °/min; Transmission electron micrographs (TEM) were taken with a HITACHI H-800 electron microscope. The powder sample of PS/laponite nanocomposites was embedded in epoxy and ultrathin-sectioned (the ultrathin sections were about 60 nm). Scanning electron microscopy (SEM) was performed on a HITACHI-520 electron microscope. The natural fractures of samples were coated with gold and observed directly. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TG-40 thermogravimetric analyzer under N₂ flow. The heating rate was 15 K/min. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 thermal analyzer with Ar protection, and the temperature rate was 20 K/min.

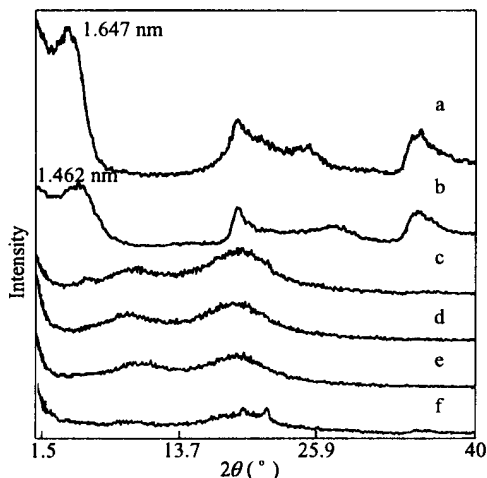


Fig. 1 XRD patterns of organo-laponite (a) laponite (b) and PS/laponite nanocomposites containing 2 wt% (c) 5 wt% (d) 7 wt% (e) and 10 wt% (f) organo-laponite, respectively

RESULTS AND DISCUSSION

The XRD patterns of pure laponite, organo-laponite and PS/laponite nanocomposites with different organo-laponite contents were shown in Fig. 1. The interlayer distance of the laponite increased from 1.462 nm to 1.647 nm after CTAB modification (Fig. 1, a, b), indicating the CTAB was intercalated into the gallery of laponite by cation exchange process, and made laponite organophilic. However, the characteristic d_{001} diffraction peak of the organo-laponite disappeared in the case of PS/laponite nanocomposites (with the organo-laponite weight amount of 2%, 5%, 7%, and 10%, respectively, Fig. 1c–f), which suggested the laponite layers were exfoliated by the styrene polymerization, and dispersed randomly in the PS matrix. Generally, the enthalpy gained in the styrene polymerization process led to the exfoliation of laponite layers.

TEM can be used to confirm the results obtained by XRD about the organization of the clay layers in the nanocomposites. Figure 2 shows the TEM micrographs of PS/laponite nanocomposites (with organo-laponite weight content of 5% and 10%). The dark lines corresponded to the laponite nanolayers. It can be clearly seen that the laponite monolayers and primary particles (containing several laponite monolayers) were obtained, which indicated the laponite layers were exfoliated because of the styrene polymerization in the laponite gallery. Moreover, it was clear that the exfoliated laponite primary particles, most of which ranged from 1 to 10 nm in lateral dimension, were dispersed randomly in the PS matrix. TEM micrographs confirm the XRD results that the exfoliated PS/laponite nanocomposites were prepared in this paper.

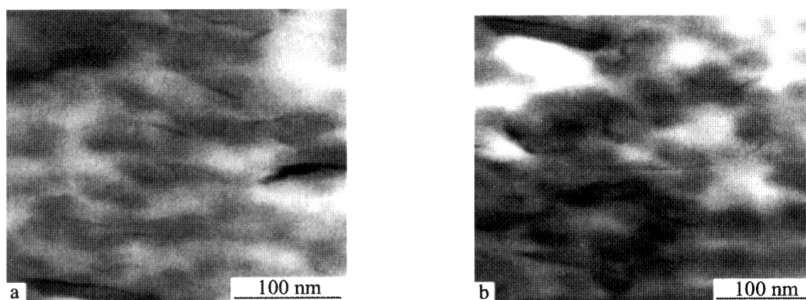


Fig. 2 TEM photographs of the exfoliated PS/laponite nanocomposites containing 5 wt% (a) and 10 wt% (b) organo-laponite, respectively

Figure 3 shows the SEM results for PS/laponite nanocomposites containing 5 wt% organo-laponite. It can be clearly seen that nanoscale spherical particles with sizes of about 120 nm were obtained. Furthermore, the particle sizes were almost monodispersed except for few aggregates with larger sizes.

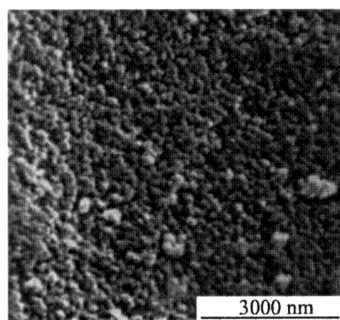


Fig. 3 SEM photographs of PS/laponite nanocomposite (containing 5 wt% organo-laponite)

The thermal stability of PS and PS/laponite nanocomposites containing different amounts of organo-laponite is shown in Fig. 4. The onset degradation temperatures of the nanocomposites containing 5 wt% and 10 wt% organo-laponite were about 322°C and 329°C, respectively. Obviously, the nanocomposites had higher thermal stability compared to PS, which degraded at 310°C, and the onset degradation temperature of nanocomposites increased with the increase of organo-laponite content. This may have resulted from the interaction between PS and laponite nanolayers, or from the presence of constrained regions in the nanocomposites.

Figure 5 shows the DSC results of both PS and PS/laponite nanocomposites. The glass transition temperatures (T_g) of PS and nanocomposites containing 5 wt% and 10 wt% organo-laponite were about 100°C, 106°C and 116°C, respectively. This T_g increase indicated that there was a strong interaction between the PS matrix and laponite nanolayers, and because of this, mobility of the PS chains near the interface became suppressed.

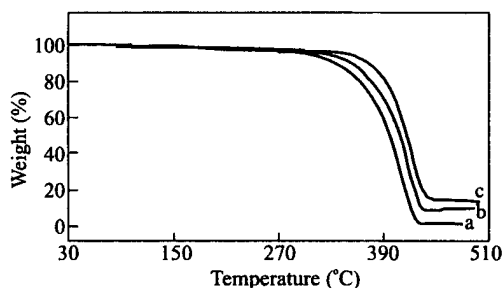


Fig. 4 TGA thermograms for PS (a) and PS/laponite nanocomposites containing 5 wt% (b) and 10wt% (c) organo-laponite, respectively

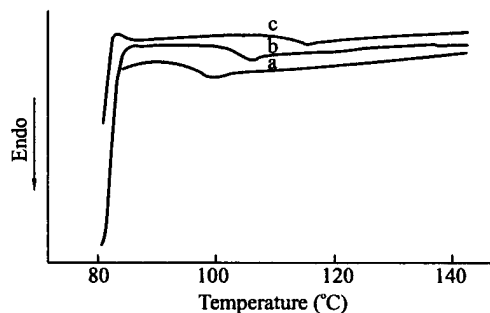


Fig. 5 DSC thermograms of PS (a) and PS/laponite nanocomposites containing 5 wt% (b) and 10 wt% (c) organo-laponite, respectively

CONCLUSION

Exfoliated PS/laponite nanocomposites were prepared successfully. The characteristic d_{001} diffraction peak of organo-laponite disappeared in the XRD patterns of nanocomposites, indicating that the laponite layers were exfoliated and the ordered crystal structure of laponite was destroyed because of the styrene polymerization. TEM also demonstrated that exfoliated PS/laponite nanocomposites were obtained, and showed that the exfoliated laponite primary particles were dispersed randomly in the PS matrix of lateral dimensions from 1 nm to 10 nm. SEM showed that the PS/laponite nanocomposite particles were almost monodispersed spheres with a size of 120 nm. Due to the interaction between PS and laponite nanolayers, the nanocomposites exhibited higher thermal stability and glass transition temperature when compared to pure PS.

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