

Synthesis and Properties of Poly(ester ether) Multiblock Copolymers/Organomontmorillonite Hybrid Nanocomposite

CHUN-CHENG LI, DONG ZHANG, ZHEN-YI LI

State Key Lab of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: In this article, poly(ester ether) multiblock copolymer/organomontmorillonite hybrid nanocomposites were prepared via an intercalation polymerization process. The resulting hybrid nanocomposites were characterized by X-ray diffraction, differential scanning calorimeter, and transmission electron microscopy. The results proved that the organomontmorillonite (organo-MMT) could be exfoliated into ~ 50 -nm thickness and dispersed in the poly(ester ether) multiblock copolymer (TPEE) matrix during the intercalation polymerization process. TPEE/organo-MMT nanocomposites showed excellent mechanical properties compared with the unfilled TPEE. When the organo-MMT content was about 3–5 wt %, MMT could enhance the strength, modulus, and hardness of TPEE without sacrificing its elongation at break. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1716–1720, 2002; DOI 10.1002/app.10552

Key words: block copolymers; elastomers; organoclay; nanocomposite

INTRODUCTION

Nanocomposites are a relatively new kind of material that exhibit ultrafine phase dimensions, typically in the range of 1–100 nm. Because of the nanometer-size effect, the nanocomposites have some unique mechanical, thermodynamic, electric, magnetic, or optical properties with respect to their conventional microcomposite counterparts. Adopting the lamellar MMT as an inorganic phase, Qi et al.^{1–4} synthesized several nanocomposites via intercalation polymerization process, and the properties of nanocomposites were improved substantially.

Poly(ester ether) multiblock copolymer is one of the most important thermoplastic elastomers

suitable for use under high loads and resist creep, is operational over a broad service temperature range without significant change in properties, and is chemical-resistant. It has been extensively used in automotive parts, electrical products, and so on.⁵ It could also be used as a modifier to enhance the toughness of poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT).^{6–7} To further improve the properties of poly(ester ether) multiblock copolymer (TPEE), the TPEE/organo-montmorillonite (organo-MMT) nanocomposites were synthesized in this article; the crystallization behavior, the mechanical properties, and nanoscale morphology were also investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods. The results indicated that TPEE/organo-MMT nanocomposites have a potentiality for industry.

Correspondence to: Z.-Y. Li (lizy@infoc3.icas.ac.cn).

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EXPERIMENTAL

Materials

Na⁺-MMT with a cation-exchange capacity of 100 mequiv/100 g and a nominal particle size of 40 μm was obtained from Institute of Chemical Metallurgy, Chinese Academy of Sciences (China). Dimethyl terephthalate (DMT) was a commercial product from Mitsubishi Chemical Corp. (Japan). Polytetramethylene glycol (PTMG, $M_w = 2000$) and 1,4-butanediol (BD) were industrial products from DuPont Co.

Synthesis

Preparation of Organo-MMT

Na⁺-MMT was dissolved in distilled water with a concentration of about 5 wt % and excess hexadecyltrimethyl ammonium bromide was added. The mixed solution was stirred for 1 h at 80°C, filtered at room temperature, and then repeatedly washed with distilled water to a very low concentration of Br⁻, where no white precipitate was observed in the filtrate when tested by a 0.1N AgNO₃ solution. The product obtained was then vacuum-dried to a constant weight at ambient temperature and ground into powder (organo-MMT).

Synthesis of Poly(ester ether) Multiblock Copolymer

Into a reactor vessel were placed 830 parts by weight of BD, 675 parts by weight of a PTMG, 842 parts by weight of DMT, a phenolic antioxidant, and a titanate catalyst. The mixture was heated to about 180°C, whereupon methanol was generated. After the theoretical amount of methanol was removed, the pot temperature was increased to about 250°C, and a vacuum was applied (<0.1 mm Hg) to produce the TPEE. The ratio of hard segment to soft segment was 55 : 45 by weight.

Synthesis of TPEE/Organo-MMT Composite

A given weight of organo-MMT was dispersed uniformly in 830 parts by weight of BD in a reactor vessel, and then 675 parts by weight of a PTMG, 842 parts by weight of DMT, a phenolic antioxidant, and a titanate catalyst were added. The other steps were the same with the synthesis of TPEE.

Measurements

Differential Scanning Calorimeter (DSC)

A Perkin-Elmer DSC-7, interfaced with a BBC-Master computer via analogue to digital con-

verter, was used to detect the thermal transition and to monitor the rate of heat flow from samples during crystallization. Each sample, measuring 5 ± 2 mg, was placed in a DSC pan and heated at a rate of 20°C/min under an atmosphere of circulating dry nitrogen. To detect the crystallization temperatures of TPEE samples, this treatment was followed by cooling at a rate of 10°C/min from 240°C to room temperature to complete crystallization.

X-ray Diffraction

XRD data between 1.5 and 40° were recorded at 2°/min on a Japan D/max-RB 12 kW diffractometer by using CuKα radiation at a generator voltage of 40 kV and a generator current of 100 mA. Samples were pellets with a smooth surface.

Transmission Electron Microscope (TEM)

The samples were ultrathin-sectioned by using a microtome equipped with a diamond knife in a liquid nitrogen trap. The thin sections were 60- to 100-nm thick. Transmission electron micrographs were obtained with a JEOL-100CX by using an acceleration voltage of 100 kV.

Mechanical Testing

The tensile and flexural testing was carried out on a universal tester (Instron 1122) on the basis of National Standard Testing Methods GB 1040-79 and GB 1042-79, respectively. The tensile strength was measured at a crosshead speed of 50 mm/min; the flexural strength and modulus were

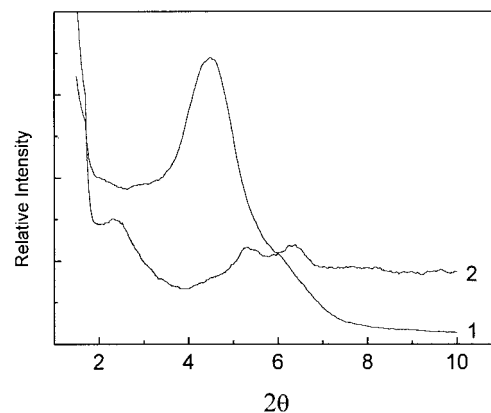


Figure 1 XRD patterns of organo-MMT and TPEE/organo-MMT composite.

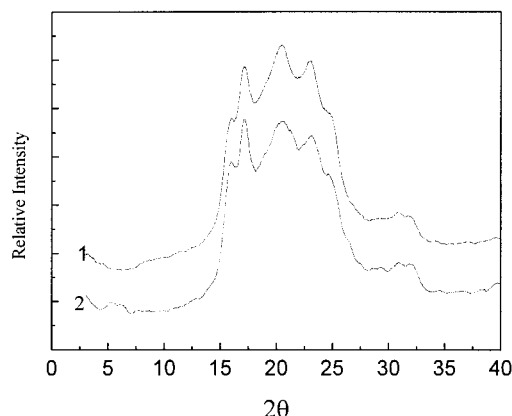


Figure 2 XRD patterns of TPEE and TPEE/organo-MMT composites.

measured at a crosshead speed of 2 mm/min. The average values of at least five tests were reported.

RESULTS AND DISCUSSION

The XRD patterns of organo-MMT and TPEE/organo-MMT composite are shown in Figure 1. The XRD pattern of organo-MMT contained a peak at $2\theta = 4.62^\circ$, whereas TPEE/organo-MMT composite showed a peak at $2\theta = 2.58^\circ$, which were basal reflections from the silicate layers. The gallery distance can be calculated according to the Bragg equation to be 1.91 nm for organo-MMT and 3.42 nm for the TPEE/organo-MMT composite; the result above indicated that TPEE molecules had intercalated into the galleries of organo-MMT.

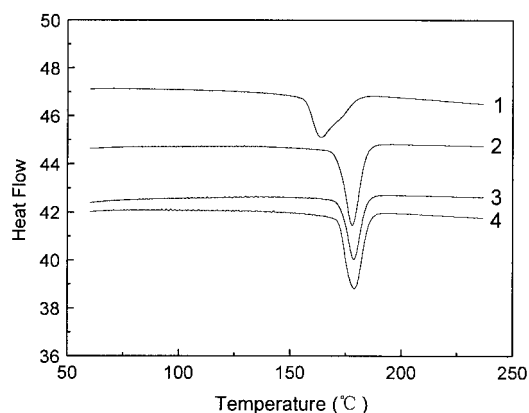


Figure 3 DSC cooling scans of TPEE and TPEE/organo-MMT composites.

Table I The Crystallization Temperature of TPEE and TPEE/Organo-MMT Composites

Organo-MMT content (wt %)	0	1	3	5
Crystallization temperature (°C)	163.9	178.0	178.7	179.0

Qi et al.⁸ reported that the presence of MMT in the PA 6/MMT nanocomposites could induce γ -form crystal of PA 6. The XRD patterns of TPEE and TPEE/organo-MMT composite are shown in Figure 2. The results above showed that the MMT did not change the positions and strength of the diffraction peaks of TPEE, which meant that MMT did not affect the crystal structure of TPEE, being different from that of PA 6/MMT nanocomposites.

DSC cooling scans at a rate of $10^\circ\text{C}/\text{min}$ of TPEE and TPEE/organo-MMT composites with different MMT contents are shown in Figure 3. The crystallization temperature of TPEE and TPEE/organo-MMT composites are listed in Table I. The DSC result showed that all samples had one exothermic peak, but the crystallization temperature and shape of the crystalline peak had changed obviously. The presence of MMT in the nanocomposites increased the crystallization temperature of TPEE and narrowed the width of the crystalline peak; meanwhile, the more the MMT, the higher the crystallization temperature of TPEE. The result above meant that MMT could act as heterogeneous nuclei of TPEE, which ac-

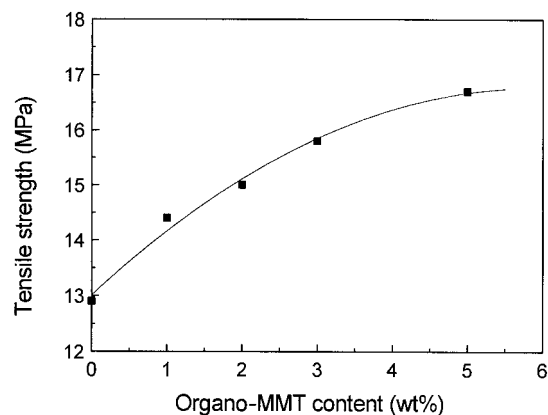


Figure 4 The tensile strength of TPEE/organo-MMT composites.

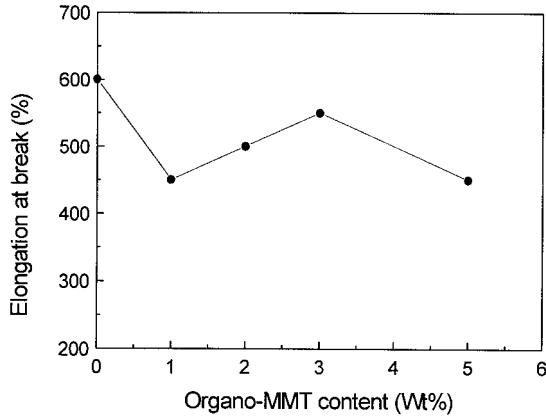


Figure 5 The elongation at break of TPEE/organo-MMT composites.

celerated the rate of crystallization of TPEE greatly.

The tensile strength and elongation at break of TPEE/organo-MMT composites are shown in Figures 4 and 5, respectively. With increasing organo-MMT content, the TPEE/organo-MMT composites showed a substantial improvement in tensile strength compared to unfilled TPEE. Figure 5 illustrates that the elongation at break of TPEE/organo-MMT composites had a slight decrease in comparison with that of pure TPEE; when the content of organo-MMT was 3 wt %, the elongation at break of composite was 550%, which was close to that of pure TPEE.

The flexural strength and flexural modulus of TPEE/organo-MMT composites are shown in Figure 6. When the organo-MMT content was above 3 wt %, the flexural strength and flexural modulus

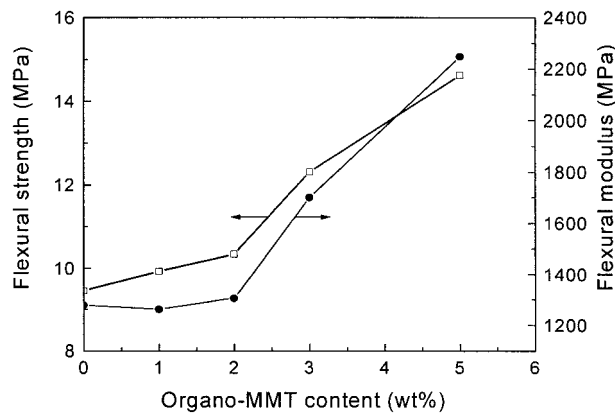


Figure 6 The flexural properties of TPEE/organo-MMT composites.

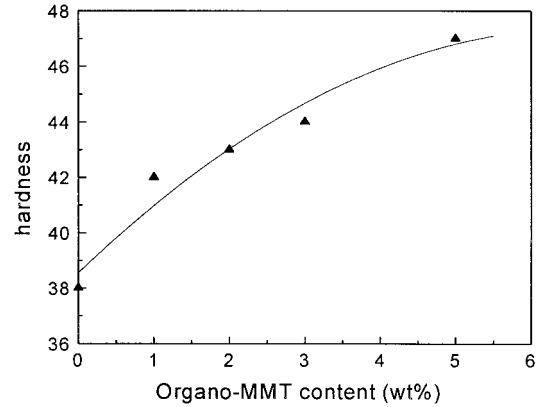


Figure 7 The hardness of TPEE/organo-MMT composites.

of TPEE/organo-MMT composites were greatly improved. Figure 7 illustrates the Shore-hardness of TPEE/organo-MMT composites was enhanced step by step with increasing organo-MMT content.

From the results above, it can be concluded that MMT could enhance the strength, modulus, and hardness of TPEE with less influence on its elongation at break, when the organo-MMT content was about 3–5 wt %.

Figure 8 shows TEM photographs of an ultra-thin section of the TPEE composition with 5 wt % of organo-MMT. The bright field in the photographs is the polymer matrix, the darker field is silicate layers which were dispersed in the TPEE matrix. From Figure 8(a), it can be clearly observed that organo-MMT layers were dispersed in TPEE matrix uniformly with about 50 nm thickness. The photographs of Figure 8(b) clearly show that the structure of MMT was similar to that of unintercalated MMT, but the interlayer distance (3–4 nm) of organo-MMT was greatly improved. The result above proves that the TPEE chain had intercalated into the galleries of organo-MMT. It was consistent with that of XRD.

CONCLUSION

1. Organo-MMT particles could be exfoliated into ~ 50 nm thickness and uniformly dispersed in the TPEE matrix.
2. TPEE molecules could be intercalated into the galleries of organo-MMT. The interlayer distance of organo-MMT expanded because of the polymer intercalation.

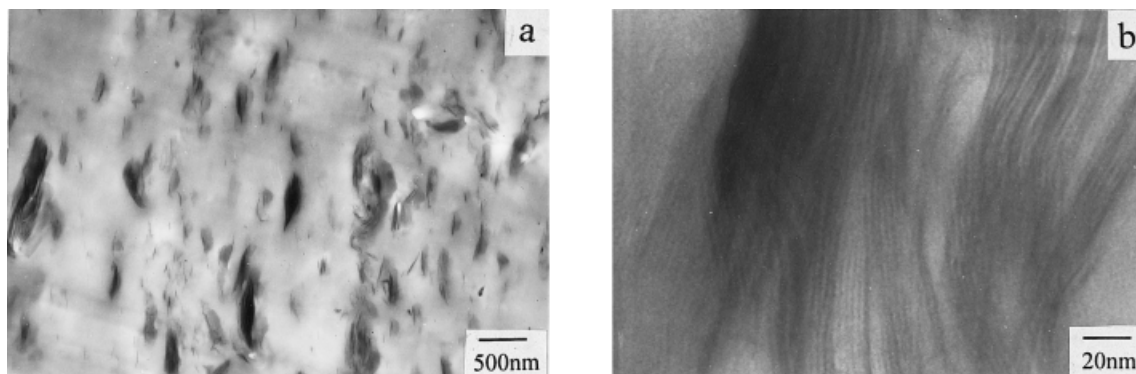


Figure 8 Transmission electron micrographs of the TPEE/organo-MMT composites with weight ratio of 100 : 5.

3. MMT could act as heterogeneous nuclei of TPEE, which made the rate of crystallization of TPEE improve greatly.

4. TPEE/organo-MMT nanocomposites showed excellent mechanical properties compared with the unfilled TPEE. When the organo-MMT content was about 3–5 wt %, MMT could enhance the strength, modulus, and hardness of TPEE without sacrificing its elongation at break.

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