Preparation and Characterization of PET/Silica Nanocomposites

Wentao Liu, Xingyou Tian, Ping Cui, Yong Li, Kang Zheng, Ye Yang

Institute of Solid State Physics, Chinese Academy of Sciences, 230031, Hefei, China

ABSTRACT: Poly(ethylene terephthalate) (PET)/silica nanocomposites were fabricated by direct polymerizing PET monomer dispersed with organic modified silica nanoparticles. The characteristics and properties of these nanocomposites were investigated by the transmission electron microscopy, differential scanning calorimetry, and thermogravimetric analysis, respectively. The results show that (1) the nanoparticles have been well dispersed in the polymer matrix; (2) the addition of nanoparticles can speed up the crystallization and melting point; and (3) the addition has no significant effect on the synthesis process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1229–1232, 2004

Key words: poly(ethylene terephthalate); silica; nanocomposites; crystallization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a widely used material in high gas barrier fields because of its low cost and good mechanical properties. There were many approaches to enhance the gas barrier property. For example, improving PET by a small amount of aromatic monomer,[1–3] incorporating PET with talc platelets[4] or clay,[5] blending PET with thermotropic liquid crystalline polymer (TLCP),[6] treating the surface of PET film with argon plasmas,[7] and coating the surface of PET film with thin layers of compact Al_2O_3[8] can improve the gas barrier property. However, none of these methods have been used industrially because of the cost and complex synthetic technologies as compared to that of the pure PET. Another important problem with these techniques is the reduction of clarity after PET modification.

Recently, the composites of polymer/inorganic nanoparticles have attracted more and more attention than in the past decades and have made great progress. According to Nielsen′s model,[9] filling the polymer with inorganic nanoparticles can effectively decrease the gas permeability because the particles are impermeable. In addition, nanofiller can serve as a nucleating agent to speed up crystallization and to increase crystallinity, which reduces the permeability according to the two-phase model.[10–12] Many researchers have been trying to enhance the gas barrier properties by addition of nanoparticles. However, few reports related to PET/inorganic particle nanocomposites have been published. Up to now, dispersion of nanoparticles and fabrication remains an unsolved problem.

In the present study, the preparation of PET/silica nanocomposites is systematically studied. The dispersion, thermal properties, and melting behaviors of the nanocomposites were characterized by means of transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), respectively.

EXPERIMENTAL

Materials

Organic modified silica was purchased from Zhoushan MingRi Nanomatrial Ltd. Co. (Zhejiang, ZhouShan, China). Terephthalic acid (PTA), ethylene glycol (EG), and antimony acetate (as catalyst) were kindly supplied by Changzhou Huayuan Radics Ltd. Co. (Jiangsu, China).

Preparation of PET/silica nanocomposites

The nanocomposites were fabricated with homemade equipment. The organic modified silica were dispersed in the solution of EG by ultrasonic vibration for 5 min at room temperature; the weight ratio of silica/EG is 2 : 5. Then, the solution of silica and EG, 55 g for PET/0.5 wt % silica and 290 g for PET/2.5 wt % silica, respectively, was mixed with PTA, EG, and antimony acetate

TABLE I
Fundamental Properties of the Samples

Specimen	IV (dl/g)	COOH%	Lucency	B*
Pure PET	0.652	15.5	65.3	6.5
PET/0.5 wt % silica	0.645	14.1	66.2	6.2
PET/2.5 wt % silica	0.658	14.4	67.2	6.6

(250 ppm antimony, based on the polymer). The mixture was agitated at 30 rpm before heating at room temperature. The mixture was then heated in nitrogen atmosphere from room temperature under a pressure of 3.0 kg to esterify it. In this condition, the esterification appears at 250–260°C. After completed esterification, the pressure was reduced to air pressure to emit the water generated during the esterification. Afterward, the polymerization was carried on at 260–270°C under a pressure of 200–300 Pa to drain out the excess EG. A power meter was used to denote the polymerization level. When the output power changes 10% (it takes about 1 h for each sample), we decrease the pressure to less than 20 Pa and continue to agitate the mixture. When the power meter increases from 10% to 80%, for each sample, time has little difference; with changes from 60 to 90 min, the agitation was stopped. Finally, the melting polymer was extruded through an orifice at the N_2 pressure of 3.0 kg and cooled with water. The pure PET, PET/0.5 wt % silica, and PET/2.5 wt % silica were fabricated by the same process.

Characterization of PET/silica nanocomposites

The intrinsic viscosity (IV), content of diethylene glycol (DEG), and carboxylic radical, lucency, and color parameter of PET/silica nanocomposites were measured. For the IV measurement, 250 ± 5 mg nanocomposite is introduced in 100-mL solution of phenol and tetrachloroethane (weight ratio is 3 : 2). The intrinsic

viscosity was extrapolated from the time of outflow, which was measured by a Ubbelohde viscometer.

After the nanocomposites were saponified by sodium hydroxide and methanol, the content of DEG was measured on an HP6890 gas chromatograph.

The specimens for TEM observation are sliced at −80°C with an Ultracut Uct microtome. The TEM observation was carried out with a Jeol 100CX II TEM.

The thermal properties of the nanocomposites were examined with a Pyris-1 Perkin–Elmer DSC. The temperature of the instrument was calibrated with indium and the baseline was checked by using sapphire. All tests were performed in nitrogen atmosphere. Before each measurement, the specimen was first heated to 550 K with a heating rate of 20 K/min, then annealed at 550 K for 5 min to remove residual nuclei and to keep an identical thermal history, and finally, cooled down to room temperature. The heating rate for the measurement is 10 K/min.

TGA analyses were performed with a Pyris-1 Perkin–Elmer thermal analyzer. The results were acquired with a heating rate of 20 K/min from 20 to 600°C.

RESULTS AND DISCUSSION

The basic properties of nanocomposite

The basic properties, intrinsic viscosity, content of DEG and carboxylic radical, lucency, and color parameter of the samples are shown in Table I. The intrinsic viscosities of the three samples are approximately equal because the polymerizations were controlled by melt viscosities. It can be seen from Table I that the other data of nanocomposites are also consistent with those of pure PET, which means that the addition of nanosilica has no significant effect on the polymerization process.
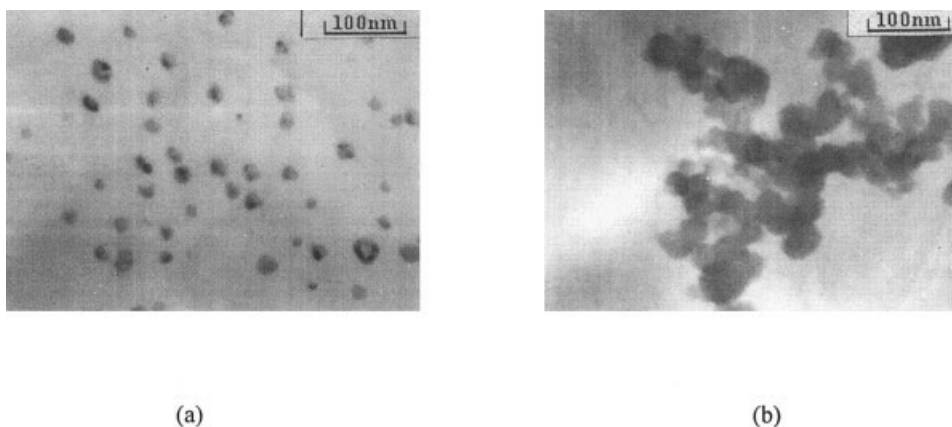

(a)

(b)

Figure 1 TEM micrograph of PET/silica nanocomposite. (a) PET/0.5 wt % silica; (b) PET/2.5 wt % silica.
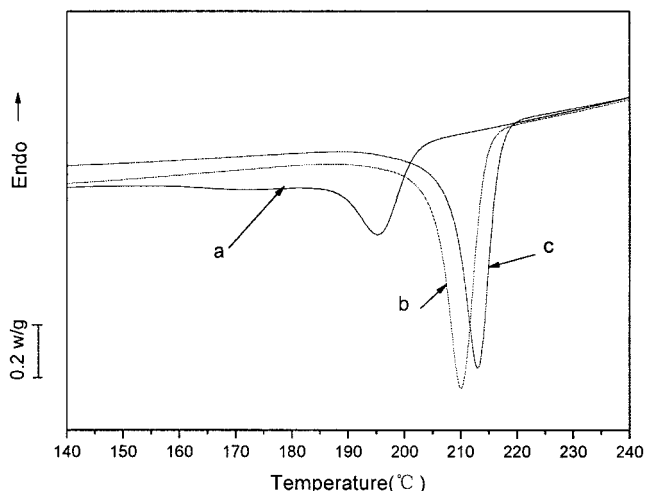
Figure 2 Cooling measurement of DSC trace for (a) pure PET; (b) PET/0.5 wt % silica nanocomposite; (c) PET/2.5 wt % silica nanocomposite.

Dispersion of nanoparticles

It is well known that the dispersion of the filled particles in the polymer significantly affects the properties of the composites. On the other hand, inorganic nanoparticles are hard to disperse in polymer matrices because of particle agglomeration and immiscibility between the inorganic particles and the polymer matrix. Although PET polymer is hydrophobic, the silica and monomer (ethylene glycol) of PET are hydrophilic, which will improve the compatibility of silica and PET. Use of monomer hydrophilicity did result in good dispersion in the present study. The nanoparticles were initially dispersed in EG by ultrasonic vibration. The PTA is compatible with the solution
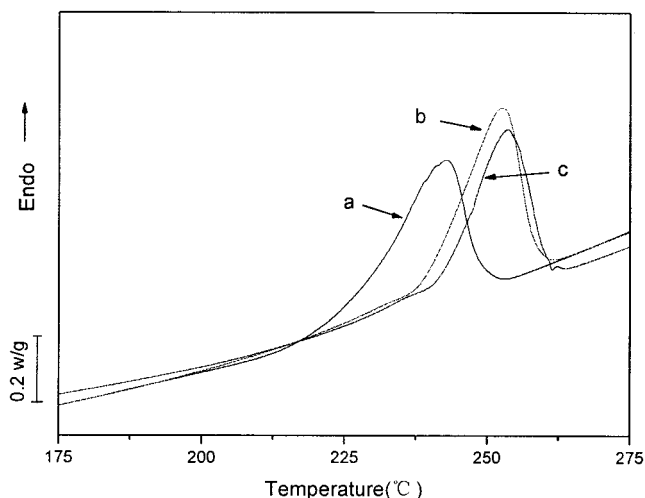

Figure 3 Heating measurement of DSC trace for (a) pure PET; (b) PET/0.5 wt % silica nanocomposite; (c) PET/2.5 wt % silica nanocomposite.

TABLE II
Thermal Property Data

Specimen	T_g (°C)	T_c (°C)	FWHM (K)	T_m (°C)
Pure PET	73.8	195	8.26	243
PET/0.5 wt % silica	81.5	210	5.61	252
PET/2.5 wt % silica	83.4	213	4.63	254

above 200°C. Finally, a good dispersion of silica in the polymer matrix is obtained as shown in Figure 1. The nanoparticles were well dispersed in the polymer matrix when the concentration of the filler is low and the average size of particles is about 30 nm, as shown in Figure 1(a). However, the dispersion is inhomogeneous and some aggregations can be found in high concentrations of the filler; the average size of the particles is about 60 nm, as shown in Figure 1(b). It is reasonable to think that for high-concentration silica nanoparticles, the distance of the particles is small, so these particles are easy to aggregate. This result indicates that high concentration of filler is not beneficial for dispersing nanoparticles to polymer matrix.

Effect of nanoparticles on the thermal properties

Rong et al.[13] have shown that the addition of silica nanoparticles has no significant effect on the crystallization process and the crystallization temperature of polypropylene (PP). However, other scientists[14–21] such as Chi et al.[22] have reported that particles increase the rate of crystallization in polymer. In this study, it is found that filling PET with silica nanoparticles results in somewhat of a change in the thermal properties. Figures 2 and 3 are the DSC traces with the cooling and heating measurements, respectively. The data of thermal properties listed in Table II are calculated from Figures 2 and 3. It can be seen that filling PET with silica nanoparticles will increase the crystallizing temperature by 15°C for PET/0.5 wt % silica and 18°C for PET/2.5 wt % silica, respectively. The melting points of PET/0.5 wt % silica and PET/2.5 wt % silica are higher than that of pure PET by 9 and 11°C, respectively (as shown in Fig. 3). It is thought that the increase in T_m may result from the well-dispersed nanoparticles that make the PET segment form more perfectible crystals during the crystallization. Mucha et al.[23] reported that the increase in T_m in PP/carbon black was caused by some hindrance at the beginning of the melting process. However, we think that this hindrance cannot cause as big an effect on T_m as that of our samples.

Figure 4 shows the TGA results. It can be seen from the curves that the thermolysis temperature of PET/silica shifts to a higher temperature than that of pure PET. Even at a small addition of nanoparticles, there is an obvious increase in thermolysis temperature. This
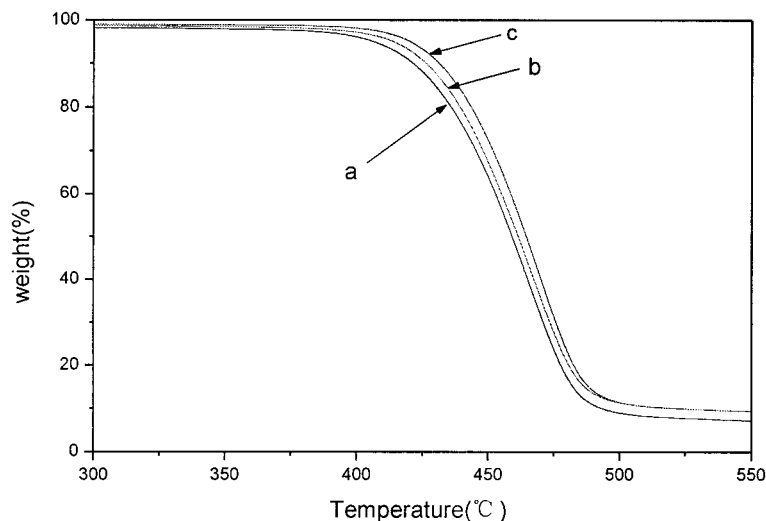
Figure 4 Thermogravimetric analysis (TGA) curves for (a) pure PET; (b) PET/0.5 wt %silica nanocomposite; (c) PET/2.5 wt % silica nanocomposite.

fact indicates that there is a strong interaction between the particles and polymer matrix. Similar results of high thermolysis temperature of intercalated PS/clay nanocomposite were reported by Fu[24] and Doh.[25] It can be found that there are greater residue weights of the two composites than that of pure PET. These additional weights should be undecomposed filler of silica within this range of temperature.

CONCLUSION

In this article, PET/silica nanocomposites were successfully fabricated by *in situ* polymerization. Nanoparticles can be well dispersed in the polymer matrix, and the average particle size in PET is about 30 nm for 0.5 wt %. The addition of nanoparticles increases the crystallizing temperature and melting point of the polymer. The addition of nanoparticles does not affect the process of synthesizing pure PET very much.

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