

Preparation, Crystallization, and Spinnability of Poly(ethylene terephthalate)/Silica Nanocomposites

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ABSTRACT: Poly(ethylene terephthalate) (PET)/silica nanocomposites were successfully prepared by *in situ* polymerization. Silica nanoparticles were uniformly dispersed in the process of polymerization. By means of hot-stage polarization microscope and DSC, the influence of nanosilica on the crystallization of PET/silica nanocomposites has been clarified. The results show that nanosilica does not behave as a nucleating agent in PET but postpones the

appearance of crystallite. This phenomenon is very favor to improve spinnability. The investigation on melt spinning of PET/silica nanocomposites also shows that it is advantageous to spinning with descending the spinning temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2564–2568, 2007

Key words: PET; nanosilica; crystallization; spinnability

INTRODUCTION

In recent years, with the development of nanoscale materials and technologies, the composites of polymer/inorganic nanoparticles have attracted a great attention from investigators worldwide because by the addition of a few percent of inorganic nanoparticles to a polymer matrix, the resulting nanoscale composites have been found to exhibit significant improvements in many properties.^{1–3}

Poly(ethylene terephthalate) (PET) is a material with low cost and high performance that has found wide applications in the fields of fibers and nonfibers.^{4,5} There has been much research on modification PET mainly focused on PET/inorganic nanoparticles composites and some of which have already been applied in plastic industries. However, few reports related to PET/nanosilica^{6,7} fibers have been published. To prepare PET/nanosilica fiber, the key is to prepare chips that nanosilica is well-dispersed in polymer matrix. Until now, many ways about dispersion of nanoparticles have been reported⁸ but it remains an unsolved problem. In this article, a novel method⁹ with low cost and industrial availability is adopted and nanosilica could be well-dispersed in the PET by *in situ* polymerization.

As we know, crystallization behavior plays an important role in preparing PET/nanosilica fibers. It has been reported that nanosilica serves as a nucleating

agent in PP and PA6.^{9–15} It will be unfavorable for spinning if nanosilica increases crystallization rate of PET. So, in this article, the effect of nanosilica on the crystallization behavior of PET would be studied.

The objective of this study is to prepare PET/silica nanocomposites. Dispersion of nanosilica in EG, crystallization, and thermal properties were characterized by light scattering instrument, polarizing microscopy, DSC, respectively. PET/nanosilica fibers were also prepared by industrial spinning experiments. Spinnability was investigated in the process of high speed spinning.

EXPERIMENT

Materials

Nanosilica with the particle diameter: 20–80 nm. Terephthalate acid (PTA) was kindly supplied by Sinopec Yizheng Chemical Fiber. Ethylene glycol (A. R.), antimony acetate (as a catalyst), and triethyl phosphate (TEP) (as a thermal stabilizer) in the polymerization were purchased from the market.

Preparation of PET/silica nanocomposites

Dispersion of nanosilica in EG

Different kinds of nanosilica were dispersed in the solution of EG. When the nanosilica reaches the maximal critical concentration with continuous addition, three kinds of phenomena can be observed: (1) The appearance of gel is obvious and reversible; (2) Gel never occurs and only slurry can be found; (3) Gel

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TABLE I
Composites and Intrinsic Viscosity of
PET/Nanosilica Composites

Samples no.	Content of nano-SiO ₂ (wt %)	Intrinsic viscosity (dL/g)
1	0	0.640
2	0.1	0.764
3	0.1	0.650
4	0.1	0.746

can be observed but not reversible. In this article, only the system of nanosilica/EG that presents the first kind of phenomena can be available. This system was elastic, ivory-white and then changed to the color of Cambridge blue with the usage of high-speed cutting emulsifying machine (about 28,000 rpm). It showed that nanosilica has been uniformly dispersed in the solution of EG. Then, the system was further diluted into the desirable concentration for the polymerization.

Polymerization

The PET/silica nanocomposites were prepared by *in situ* polymerization. This polymerization consists of two processes of esterification and polycondensation respectively, in two 30-L autoclaves. The system of nanosilica/EG was diluted into right concentration for PET/0.1 wt % silica. In each polymerization, the slurry mixture of the reactants was composed of PTA, EG, TEP (30 ppm), and antimony acetate (250 ppm based on the polymer). The mixture was then heated to 250°C under nitrogen atmosphere for esterification. After that, the temperature was raised to 280°C in the polycondensation reactor under vacuum condition. The polymerization was under a vacuum of 40–80 Pa for about 2 h until the intrinsic viscosity value reaches 0.62–0.76 dL/g. The value was checked by the torque value of the agitator in the pilot reactor. Finally, the melt was extruded by nitrogen pressure, cooled with water, and then cut into pellets. The specifications of all samples synthesized are given in Table I.

Light scattering measurement

The dispersibility of nanosilica in the solution of EG was characterized with a dynamic light scattering instrument (made by Malvern Co.).

Hot-stage polarization microscopy

The specimens were cut into small slices and then heated on the hot-stage. This observation was performed with an Olympus-BX51 polarization microscopy. These samples were heated to 290°C and kept for 2 min. Then, the samples were cooled at 100°C/min,

photos were taken every second, and the temperatures at each moment were also recorded.

DSC measurement

DSC measurements were performed with a PE-7 instrument. All experiments were carried out in a nitrogen atmosphere. The samples were first heated to 290°C and kept for 3 min to remove the thermal history. Then, the samples were cooled to room temperature at 20°C/min and reheated to 290°C. T_m is considered to be the maximum of the endothermic melting peak from the heating scans, and T_c the maximum of the exothermic peak of crystallization from the cooling scans.

Melt spinning

The spinning experiments were carried out with industrial high-speed spinning machine made by Jiangsu Textile Academy.

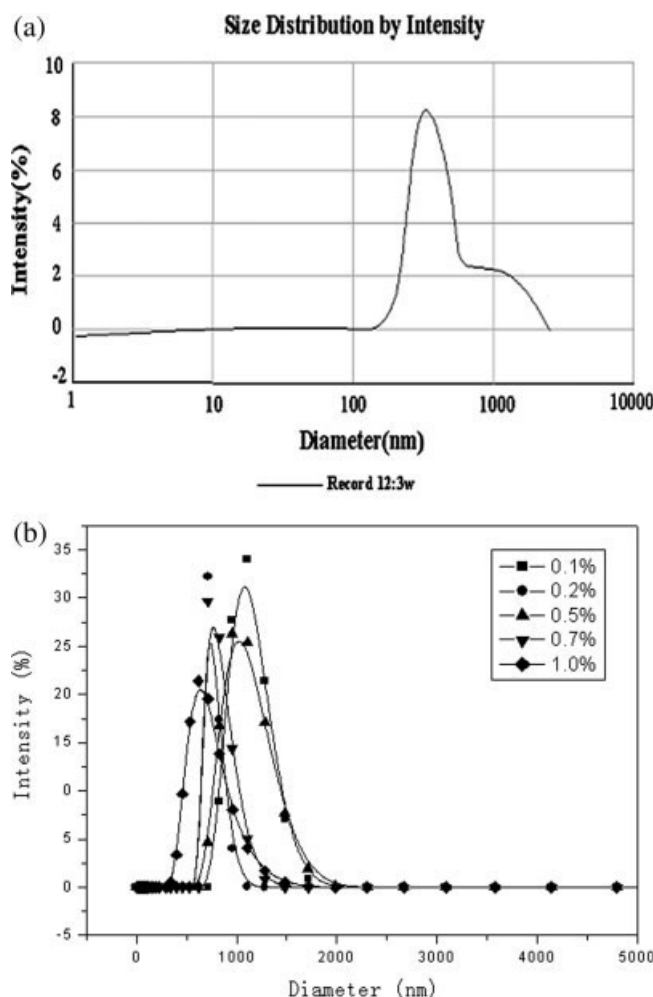


Figure 1 Measuring of equivalence particle-diameter in EG (a) nanosilica (80 nm with 0.1%), (b) different contents of nanosilica (20 nm). (a) 215.6°C; (b) 204.5°C.

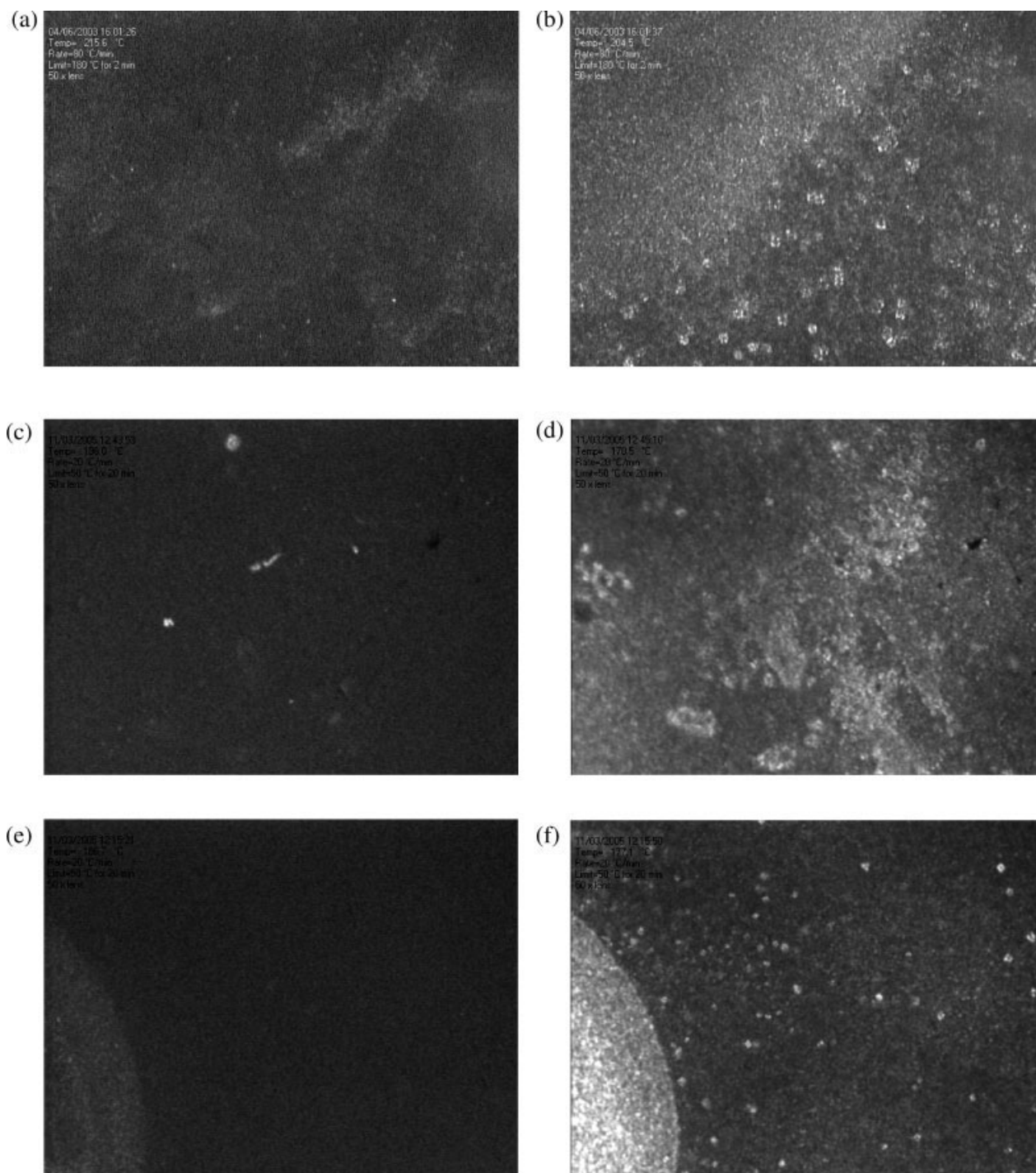


Figure 2 The temperature of the microcrystalline appearance (a) 215.6°C; (b) 204.5°C; (c) 196.0°C, (d) 170.5°C; (e) 186.0°C; (f) 177.5°C.

RESULTS AND DISCUSSION

Dispersibility of nanosilica in the solution of EG

The dispersibility of nanosilica in the solution of EG was characterized with a light scattering instrument. The dynamic light scattering technique measures the time-dependent fluctuations in the intensity of scat-

tered light that occurs because the particles are undergoing random Brownian motion. Generally, the diameter of a microparticle can be measured by dynamic light scattering instrument, based on the theory of Brownian motion. However, the Brownian motions of nanoparticles are correlative. The numerical value measured by dynamic light scattering instrument is

TABLE II
Thermal Properties of the PET/Silica Nanocomposites

Samples no.	Content of nano-SiO ₂ (wt %)	T _g (°C)	T _{cc} (°C)	T _m (°C)	T _{mc} (°C)
1	0	78.0	134.0	253.3	215.6
2	0.1	73.5	126.5	244.7	192.6
3	0.1	77.1	128.0	248.2	194.3
4	0.1	70.1	126.1	245.7	200.1

actually the “equivalent particle-diameter” of cooperative Brownian motion for many nanoparticles in solution. So here equivalent particle-diameter is adopted to characterize the interaction correlative length of nanoparticles in solution. Measuring of equivalent particle-diameter for nano-SiO₂ (80 nm with 0.1 wt %) in EG are shown in Figure 1(a). It can be found that equivalent particle-diameter is about 0.5 μm. Measuring of equivalent particle-diameter for different contents of 20 nm nanosilica in EG are shown in Figure 1(b). It shows that equivalent particle-diameter is about 1 μm.

Hot-stage polarization microscopy analysis

According to Figure 2, as the addition of nanosilica, the temperature that the first bright spot appears on the dark screen, with the microcrystallite appearing is about 20–30°C lower than that of PET. It indicates that the addition of nanosilica postpones the appearance of the microcrystalline. It may be explained as follows: as the microcrystalline appears, much of microcrystallines connect together more quickly than that of the general PET. When the crystals in the system connect together, the crystal is too little to form spherical crystal. This property is in favor of enlarging the temperature range for the filament elongation in spinning line.

Effect of nanoparticles on the thermal properties

From Table II, it can be found that the onset crystalline temperature, T_{mc} , of PET/nanosilica is lower than pure PET chip. So the addition of nanosilica postpones the crystalline temperature of PET.

From Figure 3, it can be found that the onset temperatures of crystallization for the samples with same quantities of nano-SiO₂ are close, which is lower than that of PET for 20°C in Table I.

Spinnability analysis

To eliminate experimental difference in lab, polymerization and spinning on a scale of tons have been carried out, and fundamental spinning parameters for PET/nanosilica composites are listed in Table III. It can be found that the spun temperature of PET/nano-

silica composites was 15–20°C lower than that of general PET, and the melting point of chip was about 10°C lower. It also shows spinning temperature of PET/silica nanocomposites should be decreased to make spinning to be normal. Sample 2 was prepared with the addition of nanosilica (20 nm), and the take-up velocity of POY can reach 3500 m/min. Obviously, samples with the addition of nanosilica have better spinnability than that of general PET.

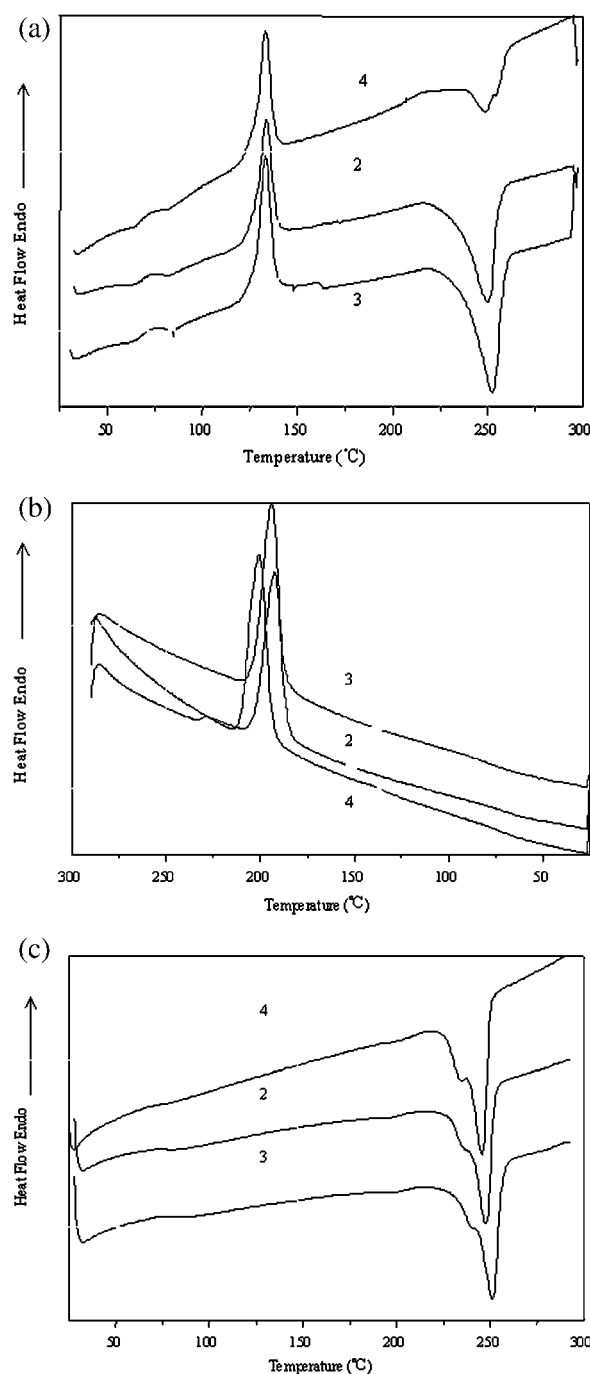


Figure 3 DSC curves of PET/silica nanocomposites. (a) Heating scans; (b) cooling scans; and (c) second heating scans.

TABLE III
Spinning Parameters for PET/Silica Nanocomposites

Sample no.	1	2	3
SiO ₂ Content (wt %)	0	0.1	0.1
Intrinsic viscosity (dL/g)	0.625	0.764	0.650
Melt point, T_m	261	249	250
Screw temperature (°C)			
I	283	220	215
II	295	275	275
III	295	275	275
IV	280	275	270
Spinning temperature (°C)	290	275	275
Spinning velocity (m/min)	3,000	3,500	3,200
Titre (D/f)	75/36	75/36	75/36
Elongation (%)	128	130	137
Strength (CN/dtex)	2.05	2.09	1.65
Spinning status	Excellent	Excellent	Excellent

CONCLUSIONS

In this study, PET/silica nanocomposites were successfully prepared by *in situ* polymerization. Nanosilica can be well-dispersed in the polymer matrix. The filling PET with 0.1 wt % nanosilica particles can result in somewhat effect on the thermal properties, and in the process of cooling, that nanosilica do not behave as a nucleating agent but rather retard the appearance of the microcrystalline, which is very favor to improve spinnability. Polymerization and spinning

on a scale of tons have been carried out and PET/silica nanocomposites have a better spinnability than that of general PET.

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