Antielectrostatic Poly(ether ester) Block Copolymer of Poly(ethylene terephthalate-*co*-isophthalate)–Poly(ethylene glycol)

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ABSTRACT: Poly(ethylene terephthalate) (PET) fiber has a low moisture regain, which allows it to easily gather static charges, and many investigations have been carried out on this problem. In this study, a series of poly(ethylene terephthalate-*co*-isophthalate) (PEIT)–poly(ethylene glycol) (PEG) block copolymers were prepared by the incorporation of isophthalic acid (IPA) during esterification and PEG during condensation. PEG afforded PET with an increased moisture affinity, which in turn, promoted the leakage of static charges. However, PET also then became easier to crystallize, even at room temperature, which led to decreased antistatic properties and increased manufacturing inconveniences. IPA was, therefore, used to reduce the crystallinity of the copolymers and, at the same time, make their crystal structure looser for increased water absorption. Moreover, PET fibers with incorporated IPA and PEG showed good dyeability. In this article, the structural characterization of the copolymers and antistatic and mechanical properties of the resulting fibers are discussed. At 4 wt % IPA, the fiber containing 1 mol % PEG with a molecular weight of 1000 considerably improved antistatic properties and other properties. In addition, the use of PEIT–PEG as an antistatic agent blended with PET or modified PET fibers also benefitted the antistatic properties. Moreover, PEIT–PEG could be used with another antistatic agent to produce fibers with a low volume resistance. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1696–1701, 2003

INTRODUCTION

Poly(ethylene terephthalate) (PET) fiber is a most important synthetic fiber with good mechanical and thermal properties, but because of its high crystallinity and poor water absorptivity, it has a low electrical conductivity. Electrostatic charges dissipate only with difficulty. To improve the antistatic properties of PET, most studies over the past 20 years have been carried out by the incorporation of dicarboxylic acid or diol as the third monomer. The resulting PET fibers showed improved hygroscopicity and antistatic properties and improved dyeability.[1–6]

Of all the third monomers investigated, poly(ethylene glycol) (PEG) has arguably been the most useful. PEG affords PET fibers with an affinity toward moisture, which greatly helps the leakage of static charges.[3–6] Sharples and coworkers believed that the high conductivity of PEG did not arise from absorbed water but from proton removal.[7,8] Bailey and Koleske, however, suggested in their book that the experimental results of Sharples and coworkers were best explained by an ionic mechanism.[9]

Another reason for the use of PEG as the antistatic agent for PET is that PEG has better compatibility with PET than do other antistatic agents. The resulting PET fibers, therefore, retain good antistatic properties after many washings.

PEG, however, also makes PET easy to crystallize, even at room temperature, so PET granules may become brittle during storage. As isophthalic acid (IPA) can destroy the regularity of PET crystallites, it may be used to reduce the crystallinity of PET.[10,11] Therefore, we prepared a series of poly(ethylene terephthalate-*co*-isophthalate) (PEIT)–PEG block copolymers by incorporating both IPA and PEG during polymerization to improve the antistatic properties of the PET fibers.

Theoretically, there are four processes to synthesize PEIT–PEG block copolymers:

1. Melt polymerization among dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG), and PEG.
2. Transesterification between PEG and polyesters at a high temperature.
3. Melt condensation between low-molecular-weight polymers.
4. PEG condensation with bishydroxyethyl terephthalate and bishydroxyethyl isophthalate (BHIT), which result from esterification among terephthalic acid (TPA), IPA, and EG.

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TABLE I
Sample Parameters

| Sample no.	Sample name	IPA (wt %)[a]	M_{PEG}	PEG (mol %)[a]	PEG (wt %)[a]
1	PET	0	—	—	—
2	PEIT	4	—	—	—
3	PEIT–PEG600-1	4	600	1	3.6
4	PEIT–PEG600-2	4	600	2	7.2
5	PEIT–PEG1000-1	4	1000	1	6
6	PEIT–PEG1000-2	4	1000	2	12
7	PEIT–PEG1000-3	4	1000	3	18
8	PEIT–PEG2000-1	4	2000	1	12

[a] All of the percentages were related to the content of TPA.

The fourth process is the most common in industrial production at present, so the PEIT–PEG copolymers examined in this study were prepared that way. In this study, we analyzed the synthesis, structural characterization, antistatic properties, and mechanical properties of these copolymers.

The common molecular formula of PEIT–PEG is as

$$\text{---}\!\!\left[\text{O(CH}_2\text{CH}_2\text{O)}_x\text{---R---(OCH}_2\text{CH}_2\text{O---R)}_y\right]\!\!\text{---}$$
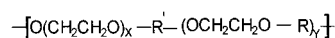
where X and Y are the lengths of EG and ethylene terephthalate (ET), respectively, and R and R′ represent
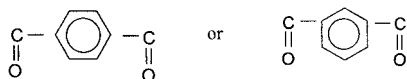
EXPERIMENTAL

Synthesis of PEIT–PEG copolymers

Synthesis was carried out in a 2-kg scale Shimpo ring-cone polymerizer (Japan), into which TPA, IPA, EG, and cobalt acetate and manganese acetate catalysts were placed. Esterification took place between 190 and 225°C, and the pressure range was from 2 to about 2.6 kg/cm³. The H_2O byproduct and surplus EG were eliminated. When the quantity of eliminated H_2O reached 70%, according to the theoretical value, the pressure was relieved. PEG with varying molecular weights and molar (or weight) fractions, antimony trioxide catalyst, and triphenyl phosphate stabilizer were added into the polymerizer with stirring at normal pressure for half an hour. Meanwhile, the temperature was raised to 275°C, and a vacuum of 10 mmHg was applied with the subsequent elimination of EG. The copolymerization process was continued until the stirring torque of the polymerizer was almost stable. A series of PEIT–PEG block copolymers was obtained with varying PEG molecular weights and molar (or weight) fractions. These copolymers are shown in Table I.

Preparation of the fibers

PEIT–PEG fibers were spun with an MSTC-400 melt spinning tester (Japan) with screw temperatures of 268, 270, and 260°C, and a spinning speed of 400 m/min. The as-spun filaments were submitted to an 3.0× draw on a Barmag 3010 drafting machine (Germany) at a hot-plate temperature of 140°C.

Analysis of the copolymerization

Because we incorporated both IPA and PEG during copolymerization, the copolymerization times varied from that of pure PET polymerization.

To analyze the copolymerization efficiency, we subjected the block copolymers to Soxhlet extraction with chloroform for 24 h to remove any unreacted PEG, polyester with a rich content of PEG, and low-molecular-weight PET and PEIT. We tested and verified the results by Fourier transform infrared (FTIR) measurement with a Nicolet Nexus-470 (USA) at 25°C, scanning 32 times with a resolution ratio of 2 cm^{-1}. The weight loss ratio (η) of the copolymers after extraction was calculated by the following equation:

$$\eta = \frac{W_0 - W_1}{W_0} \times 100\%$$

where W_0 and W_1 are the copolymer dry weights before and after extraction, respectively. A higher weight loss ratio represents a lower copolymerization efficiency.

Intrinsic viscosity of the copolymers

One important property of the synthesized copolymers, especially with regard to their spinning efficiency, was intrinsic viscosity. This was measured with an Ubbelohde viscometer in a thermostatic water bath (25 ± 0.2°C) with a solvent of 1:1 (w/w) phenol/tetrachlorethane and a solution concentration of 0.5 g/dL.

Crystallizition behavior of the copolymers

The incorporation of PEG into PET during condensation allows PET to easily crystallize even at room temperature, which is unfavorable for the antistatic properties and the manufacture of PET, so IPA was used to reduce the crystallinity of PET. To examine the crystallization of the PEIT–PEG copolymers at room temperature, we melt-pressed the samples between smooth stainless steel plates with an aluminum spacing plate 100 μm in thickness and then quenched them in liquid nitrogen. The resulting amorphous films were then crystallized at 35°C for 8 h. Wide-angle X-ray diffraction (WAXD) was performed with a Rigaku D/max-rB instrument (Japan) with nickel-filtered Cu Kα radiation.

Fiber properties

Tensile properties were determined on an Instron universal tensile testing machine (UK) with an extension rate of 250 mm/min and a gauge length of 250 mm. Volume resistance was measured on a YG-321 fiber resistance tester (China) at 20°C and 65% relative humidity.

RESULTS AND DISCUSSION

Analysis of the copolymerization time

The incorporation of IPA into the TPA–EG esterification system shortened the esterification time because of the electrophilic effect of the carboxyl weakening the cloud density of the ortho and para positions on benzene ring but strengthening that of the meta position. So the carboxyl carbon atom located in the meta position had a stronger positive charge than the other two positions, which was helpful for nucleophilic substitution between the alcohol and acid.[12] However, the addition of IPA lengthened the condensation time because the steric hindrance of BHIT made its reaction with the catalysts difficult.
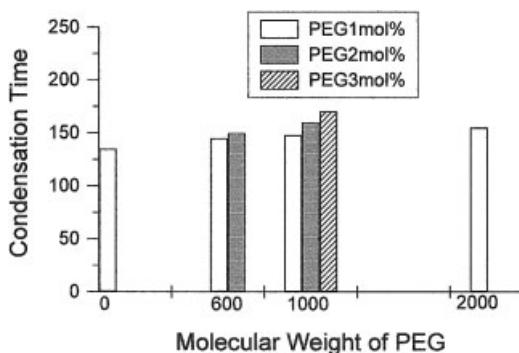

Figure 1 Relationship between the molecular weight of PEG and condensation time.

TABLE II
Weight Loss Ratio of the Copolymers After Extraction

Sample	W_0	W_1	η
1	5.012	4.985	0.54
2	5.007	4.981	0.52
3	5.009	4.965	0.88
4	5.005	4.959	0.92
5	5.001	4.938	1.26
6	5.005	4.938	1.34
7	5.010	4.916	1.88
8	5.004	4.941	1.26

The molecular weight and molar (weight) fraction of PEG also had a significant effect on the condensation time. From the results shown in Figure 1, we concluded that the condensation time rose with increasing molecular weight of PEG from 0 to 600, 1000, and 2000 at a given PEG molar fraction. This was due to the segment length increasing with increasing PEG molecular weight. The longer length prevented the functional groups from reacting with each other. When the PEG molecular weight was fixed, a larger molar fraction of PEG led to more PEG molecules taking part in the reaction, generally resulting in a longer condensation time. For 2 mol % PEG1000 and 1 mol % PEG2000, which had the same weight fraction of PEG, the condensation time decreased with increasing PEG molecular weight. This was because the number of molecules of the latter was smaller. When the molecular weight of PEG was above 4000, the condensation time increased because the longer molecular chains retarded functional group interaction with the other reacting groups. In industrial production, therefore, the molecular weight of PEG would ideally not to be too high.

Analysis of the copolymerization efficiency

PEG provided the block copolymers with more soft segments, but meanwhile, the contents of PEIT and PET with low molecular weights also increased. So the weight loss ratio, summarized in Table II, was closely correlated to the molecular weight and content of PEG. The higher the molecular weight of PEG was at a fixed molar fraction, the higher the weight loss ratio was. Also, when the molecular weight of PEG was fixed, a higher molar fraction of PEG led to a higher weight loss ratio. If the weight fraction of PEG was fixed, a higher molecular weight of PEG led to a lower weight loss ratio. Pure PET and PEIT, however, showed almost no change in the weight loss ratio.

In the FTIR spectrogram of the copolymer without extraction (Fig. 2), there was a hydroxyl end group absorption peak at 3600–3300 cm^{-1}. This was mostly caused by the unreacted PEG and low-molecular-weight polyester. Therefore, the insoluble polymer af-
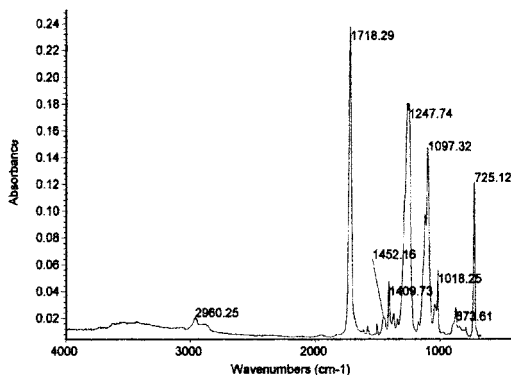
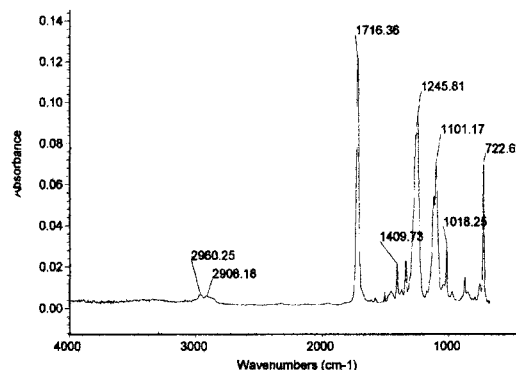**Figure 2** FTIR spectrum of sample 8 before extraction.

Figure 4 FTIR spectrum of sample 8 after extraction.

ter extraction did not exhibit that peak, as shown in Figure 3, and the extract had an obvious peak at 3419 cm^{-1}, as shown in Figure 4. Moreover, Figure 4 shows more peaks at 2970–2880 cm^{-1} than Figure 3, which resulted from the stretching-out and drawing-back movement of CH$_2$ groups. These results suggest that the extraction experiment was successful.

Copolymer intrinsic viscosity

Intrinsic viscosity is important to the spinning process. Because the incorporation of IPA and PEG into PET influenced the copolymer intrinsic viscosity, understanding their effects was important for determining whether the copolymerization was successful or not.

The incorporation of IPA resulted in an increased intrinsic viscosity, rising as shown in Table III. The intrinsic viscosity also increased with increasing PEG molar fraction at a fixed PEG molecular weight. When the weight fraction of PEG was fixed, however, the intrinsic viscosity decreased with increasing PEG molecular weight.

It is known that polymer structure is closely related to intrinsic viscosity. According to the physical meaning of intrinsic viscosity, that is, the relative size of the hydrodynamic volume of a polymer in a solvent per unit weight, copolymer molecules containing IPA have a larger hydrodynamic volume than pure PET because of the steric hindrance of IPA. The intrinsic

viscosity, therefore, increases. The effect of PEG on the intrinsic viscosity is related to the contribution of PEG to the flexibility of the copolymer segments, which can be calculated as

$$L_S = \frac{M_{PEG}}{M_S}, \quad L_H = \frac{\dfrac{M_{PEG}}{W_{PEG}} \times (1 + i)}{M_H}$$

where L_S and L_H are the lengths of EG and ET, respectively, equal to X and Y in the former molecular formula; M_{PEG}, M_S, and M_H are the molecular weights of PEG, EG, and ET, respectively; W_{PEG} is the weight fraction of PEG; and i is the weight fraction of IPA, which are both relative to the weight fraction of TPA. The equation was established on the basis of Gilding and Reed's study.[13]

From the previous equation, one can see that the length of ET decreases with increasing PEG molar fraction when the PEG molecular weight is fixed, suggesting that the molecular chains of the copolymer are more flexible, which results in a greater entanglement between the chains and a subsequently increased hydrodynamic volume. When the PEG molar fraction was fixed, the copolymer chains with higher PEG molecular weights had greater flexibility, and the intrinsic viscosity of the copolymer, therefore, increased. At a fixed PEG weight fraction, a low PEG molecular weight resulted in a higher copolymer intrinsic viscos-
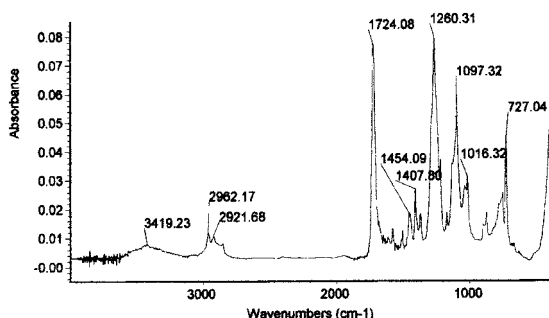

Figure 3 FTIR spectrum of the extract.

TABLE III
Intrinsic Viscosity and Lengths of EG and ET

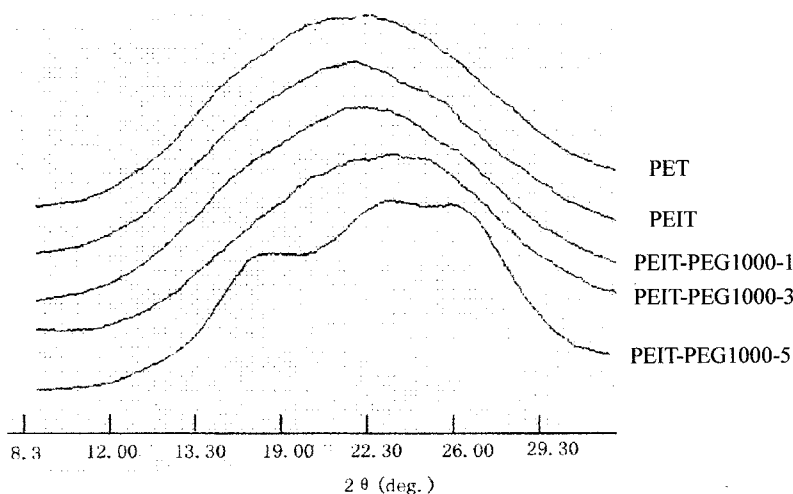| Sample	$L_S : L_H$	Intrinsic viscosity
1	—	0.650
2	—	0.732
3	14 : 104	0.650
4	14 : 52	0.687
5	23 : 104	0.704
6	23 : 52	0.735
7	23 : 35	0.762
8	45 : 104	0.718

Figure 5 WAXD curves of the copolymers.

ity because of more soft segments in the copolymer chains.

Crystallization behavior of the copolymers

Figure 5 shows the WAXD curves of samples crystallized at 35°C. In these curves, PET, PEIT, PEIT–PEG1000-1, and PEIT–PEG1000-3, did not exhibit diffraction peaks. Although PEG lowered the glass-transition temperature of PET and the segments could, therefore, easily move to crystallize, with the incorporation of IPA the copolymer crystallization was inhibited, so the copolymers were still amorphous after crystallization at 35°C for 8 h. This was useful for the antistatic properties and manufacturing processes.

Antistatic properties of the PEIT–PEG fibers (Table IV)

After the incorporation of IPA into PET, the resulting fibers had a lower volume resistance, as the amorphous region, with a greater affinity for water, increased. When the fibers contained both IPA and PEG components, the volume resistance became still lower. This was because PEG has a good affinity toward moisture. There are lone-pair electrons on the oxygen

atoms of the ether bands in the PEG molecular chains, which are bond easily with the hydrogen in the water molecules. At a fixed PEG molecular weight, a higher molar fraction induced a lower volume resistance. When the molar fraction was fixed, a higher molecular weight provided a lower volume resistance. The reason for the previous two results was that a higher content of the ether bond led to better antistatic properties. However, at a fixed PEG weight fraction, the volume resistance increased with increasing PEG molecular weight because a higher PEG molecular weight resulted in longer soft segments, which crystallized easily, reducing conductivity.

Commonly, copolymerization can decrease a polymer fiber's tenacity. This was seen in this study, as both IPA and PEG decreased the fiber strength to some degree. Riches and Haward[14] pointed out that the tensile properties of PEG block copolymers depend more on the number of hard and soft segments than on their lengths. So the mechanical properties correlated with the molar fraction of PEG rather than with its molecular weight. The higher the molar fraction of PEG was, the lower were the mechanical properties, so limiting the PEG content was necessary to preserve fiber mechanical strength.

It was further found that the use of PEIT–PEG as an antistatic agent, blended with PET or PET modified with, for example, cationic dyes or disperse dyeable PET, could yield even better antistatic properties. Moreover, PEIT–PEG could be used with other antistatic agents to produce fibers with low volume resistances.

TABLE IV
Antistatic Properties of PEIT–PEG Fibers

Sample	Volume resistance (Ω cm)	Tenacity (cN/dtex)
1	3.2×10^{14}	3.52
2	8.7×10^{12}	3.36
3	6.5×10^{11}	3.10
4	2.6×10^{11}	3.01
5	4.3×10^{11}	3.09
6	7.3×10^{10}	2.99
7	5.8×10^{10}	2.87
8	2.2×10^{11}	3.12

CONCLUSIONS

The introduction of IPA into PET increased the esterification rate but also increased the condensation time. The resulting copolymers had higher intrinsic viscos-

ities and reduced room-temperature crystallization rates. The resulting fibers had better antistatic properties.

The addition of PEG during condensation produced the following results. First, at a fixed PEG molecular weight, with increasing molar fraction, the volume resistance decreased, the copolymerization efficiency and tenacity decreased, and the condensation time and intrinsic viscosity increased. Second, at a fixed PEG molar fraction, the volume resistance decreased with increasing PEG molecular weight, and other changes were the same as mentioned previously, except that the tenacity was almost unchanged. Last, copolymers with a fixed PEG weight fraction had lower volume resistances when the PEG molecular weight was smaller; also, the condensation time and intrinsic viscosity increased, whereas tenacity and copolymerization efficiency were lower.

In a word, a lower volume resistance usually led to increased condensation time and intrinsic viscosity, decreased tenacity, and decreased copolymerization efficiency. Intermediate PEG molecular weights and concentrations produced the best overall results. In this study, at 4 wt % IPA, the fiber containing 1 mol % PEG with a molecular weight of 1000 considerably improved the antistatic and other properties.

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