

# Structure and Properties of Composite Antibacterial PET Fibers

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**ABSTRACT:** Poly(ethylene terephthalate) (PET) had been compounded with antibacterial materials for preparing antibacterial masterbatch using a twin-screw extruder. Composite antibacterial PET fibers were prepared using the antibacterial masterbatch and pure PET resin by high-speed melt-spinning device, with spinning rate 3500 m/min. The antibacterial PET fibers of 5 wt % antibacterial materials were very effective against tested germs, with antibacterial ratios more than 90%, and had well mechanical properties. Scanning electron microscopy micrograph shows that antibacterial materials have been well dispersed in PET matrix. Microstructure of compos-

ite antibacterial fibers was studied by X-ray diffraction, and the nucleating effect of antibacterial materials in the cooling crystallization process of PET was confirmed by differential scanning calorimetry (DSC). Result of thermogravimetry (TG) result shows that the addition of antibacterial materials accelerated the degradation of PET. The aged properties of antibacterial fibers were evaluated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1927–1932, 2009

**Key words:** antibacterial materials; PET; composite fibers; crystallization

## INTRODUCTION

Composite materials may show enhancement in the mechanical, thermal, optical, and physicochemical properties when compared with the pure polymer.<sup>1</sup> These enhancements attract the interest of many researchers because they lead to wider application of many polymers. Composite materials obtained using different polymer matrices have been studied. Poly(ethylene terephthalate) (PET) is one of the most large-scale products in polymer. Because of its good mechanical and optical properties, resistance to creep fracture, resistance to fatigue and wear aspects, PET is widely applied to produce fibers, films, and packaging materials with high barrier properties.<sup>2–4</sup> To date, many composite PET fibers have been researched to improve PET fibers' proper-

ties such as thermal and crystalline<sup>5–7</sup> or introduce new functional properties such as electrical conductivity,<sup>8</sup> antibacterial function,<sup>9</sup> and flame-retardant<sup>10</sup> to the fibers. Among these functional materials, antibacterial function materials have recently been a focus. When antibacterial materials are applied to PET fibers, the resultant self-sterilizing fabrics have the potential benefits of reduced disease transfer among hospital population, biowarfare protection, and other applications.

In this article, composite antibacterial PET fibers were prepared using the antibacterial masterbatch and pure PET resin by high-speed melt-spinning method. Results of our investigation on the structure of composite antibacterial PET fibers, i.e., the crystallization and morphology, were described. The antibacterial, mechanical properties, and thermal stability of composite antibacterial PET fibers were also included.

## EXPERIMENTAL

### Raw materials

Antibacterial materials used in the experiment were prepared by adsorption methodology in our

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laboratory.<sup>11</sup> An aliquot of 5 g of nano-SiO<sub>2</sub> was added into 50 mL of 0.08 mol/L silver nitrate solution. The suspended solution was adjusted to a pH value of 6–8 with NH<sub>3</sub>·H<sub>2</sub>O and was stirred at 75°C for 4 h. After adsorption reaction, the suspension was filtered with filter paper, and the sample was washed with distilled water and then dried at 110°C. Finally, Ag-loaded SiO<sub>2</sub> nanoantibacterial agent was obtained. The antibacterial materials are white powder with bulk density of 80 kg/m<sup>3</sup>.

The pure PET was purchased from Tianjin Petroleum & Chemical Corp. (Tianjin, China), which is a white powder by appearance. The coupling agent (KH-550) (H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) was purchased from Nanjing Shuguang Chemical Plant (Nanjing, China). *Escherichia coli* (*E. coli*) (ATCC 8739) and *Staphylococcus aureus* (*S. aureus*) (ATCC 6538) were provided by Shanxi Medical University (Taiyuan, China).

#### Preparation of antibacterial materials/PET masterbatch, antibacterial PET fiber

Antibacterial materials, PET resin, and coupling agent were mixed in a compounder with designed weight ratio (17 : 81 : 2 wt %) and dried at 110°C for 24 h in a regular oven, and then were extruded at 260°C by a twin-screw extruder. The diameter of screw was 35 mm, and the screw speed was 50 rpm. The extruded materials were quenched in a room-temperature water bath first and then were sliced into granules by a granulator. Finally, the antibacterial masterbatch was obtained.

Antibacterial PET fibers were spun by high-speed melt-spinning device using the antibacterial masterbatch with 17 wt % antibacterial materials and pure PET resin, with the concentration of 0%, 1.5% (1# sample), 3% (2# sample), 5% (3# sample), 7% (4# sample), 9% (5# sample), respectively. The spinning rate was 3500 m/min, and the spinning temperature was 300°C.

#### Characterization

The microstructure of composite antibacterial PET fibers and antibacterial masterbatch were observed by optical microscopy and scanning electron microscopy (SEM), respectively.

The antibacterial performance of composite antibacterial PET fibers was measured by shake flask test, according to the State Standard GB1598–1995 for the evaluation of disinfecting and antibacterial properties defined by the Ministry of Health, China. The testing method is as follows: (1) 0.75 g of fibers was placed into a 250-mL flasks with 70 mL phosphate buffer solution (PBS, 0.03 mol/L, pH 7.2–7.4) solution and 1 mL bacterial suspension, with

the concentration of germs being about 1–2 × 10<sup>4</sup> colony-forming units per milliliter (CFU/mL); (2) the flask was shaken on an agitation shaker at a speed of 300 r/min at 25°C for 1 h; (3) 1 mL of the solution before or after shaking was inoculated on a plate containing 15 mL agar; (4) the inoculated plates were cultivated at 37°C for 24 h; and (5) active bacteria were counted and antibacterial effect was calculated using the following equation:

$$R = \frac{A - B}{A} \times 100\%$$

where  $R$  is the antibacterial rate (%);  $A$  is the mean number of bacteria in the sample before shaking;  $B$  is the mean number of bacteria in the sample after shaking.

The reported results were the average values of three parallel runs.

The tensile strength and elongation at break were measured according to the National Standard of People Republic of China GB/T14344–1993. Tensile testing of samples was measured using an electronic single-fiber strength tester (YG(B)021) at the strain rate of 10 mm/min. The fiber samples were conditioned for 24 h under the standard conditions of 20°C and 65% relative humidity. The experiment was performed at a gauge length of 50 mm, using a 1 kN load cell. The final mechanical properties of all fiber samples were obtained from at least 50 reduplicate measurements.

The microstructure of composite antibacterial PET fibers was examined by X-ray diffraction (XRD) using Ni-filtered Cu K $\alpha$  radiation. 40 kV and 30 mA of voltage and current settings were used. All specimens were examined at 2 $\theta$  angles from 5° to 55°.

The crystallization behavior of antibacterial fibers was studied by differential scanning calorimetry (DSC) in N<sub>2</sub> atmosphere. The samples were first heated to 290°C and molten completely, and then were cooled to room temperature at the rate of 10°C/min. Thus, the crystallization curve of antibacterial fiber was obtained.

Thermogravimetric analysis (TGA) was performed on a STA409C instrument at the heating rate of 10°C/min in the nitrogen atmosphere.

The aged properties of antibacterial fibers were studied by artificial accelerated aging, and the methods is described as follows: PET fibers samples were exposed to artificial accelerated aging from two 30W Philips lamps in a covered chamber at room temperature, both upside and backside were irradiated together. Samples were laid parallel to the longitudinal axes of the lamps in a fixed position. The distance between light source and samples was 35 cm.

TABLE I  
The Properties of the Antibacterial PET Fiber

Sample	The content of antibacterial agent (%)	Break-down strength (cN/dtex)	Break extensibility (%)	Antibacterial rate (%)			
				<i>S. aureus</i>		<i>E. coli</i>	
				Washing 5 times	Washing 30 times	Washing 5 times	Washing 30 times
0#	0	2.09	122.0	0	0	0	
1#	1.5	2.05	123.9	39	16	28	13
2#	3	2.00	125.2	68	45	62	40
3#	5	1.98	126.0	96	86	91	83
4#	7	1.80	124.7	95	83	89	81
5#	9	1.55	125.8	96	85	90	81

## RESULTS AND DISCUSSION

### The properties of composite antibacterial PET fiber

Mechanical property of fibers is one of the important targets of the textile process and the wearing performances. The mechanical properties of the composite antibacterial PET fibers are listed in Table I.

From Table I, we noticed that tensile strength and extensibility at break of composite antibacterial fibers were changed by adding antibacterial materials. When less 5% antibacterial masterbatch were added, the tensile strength of composite fibers was decreased, but the extensibility was increased to 125.2. However, the antibacterial rate of composite fibers having same content of antibacterial masterbatch was very poor, the antibacterial rates of composite fibers containing 1.5% antibacterial masterbatch only was 39 and 28% to *E. coli* and *S. aureus*, after the content of antibacterial masterbatch was increased to 3%, the antibacterial rates were only up to 68 and 62% to *E. coli* and *S. aureus*, which decreased to 45 and 40% after washing for 30 times.

When 5% antibacterial masterbatch were added, the extensibility was increased to 126.0, which was over the virgin PET fibers; the break strength of the antibacterial fibers was decreased, but still close to the one of virgin PET fibers. However, if the added load increased, the tensile strength at break and extensibility obviously decreased, which was result from that the antibacterial materials became agglomerated when their load larger than 5% by weight in the PET, which is very harmful to mechanical property of antibacterial PET fibers.

Despite it can be found that the tensile strength of antibacterial PET decreased compare with the pure PET when more 5% antibacterial masterbatch were added, at the same time, the antibacterial rates of the composite antibacterial fibers to *E. coli* and *S. aureus* are high enough and the effect of the content of antibacterial materials to antibacterial rates was less, the antibacterial rates of all antibacterial PET fibers were up to 90% against *E. coli* and *S. aureus*,

and after washing for 30 times, the antibacterial rates were still up to 80%, which were enough to meet the need of antibacterial textiles.

The effect of the contact time on antibacterial ratios of the antibacterial fibers (3#, 4#, 5# samples) against *E. coli* and *S. aureus* is shown in Figure 1. It can be seen that the contact time of antibacterial rate increased to over 70% was 40, 20, 20 min in contact with *E. coli* or *S. aureus* for 3#, 4#, 5# samples, respectively. When the contact time was 60 min, the antibacterial rate of all samples was above 80%. Therefore, it can be concluded that the antibacterial activity of antibacterial PET was excellent.

### Morphologies of antibacterial masterbatch and fibers

The antibacterial masterbatch with 17 wt % antibacterial materials were fractured and coated with gold using a sputter coater, and then observed using scanning electron microscope (SEM). In the SEM

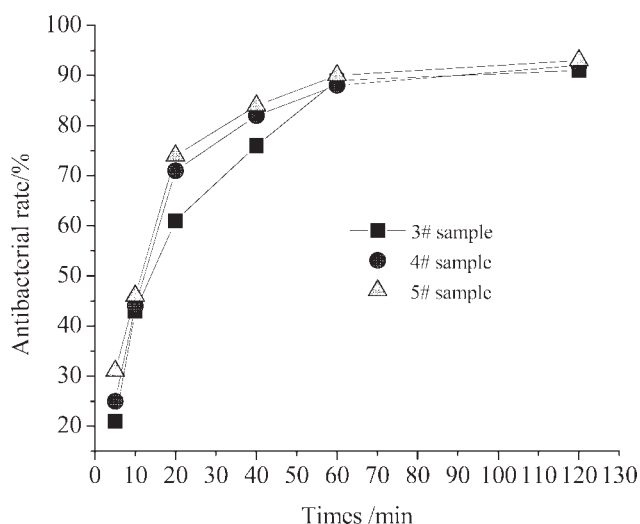
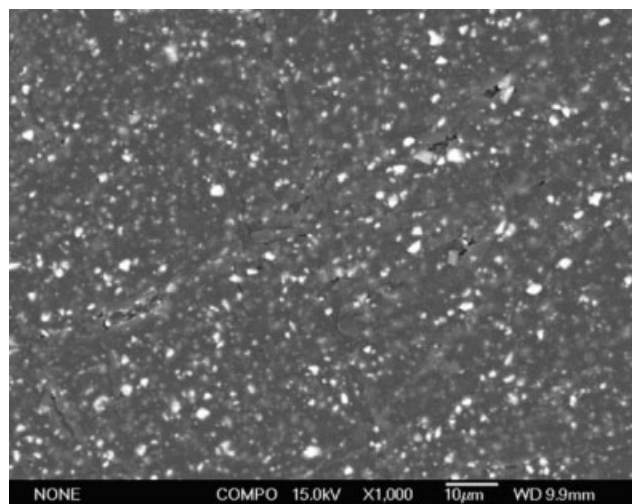


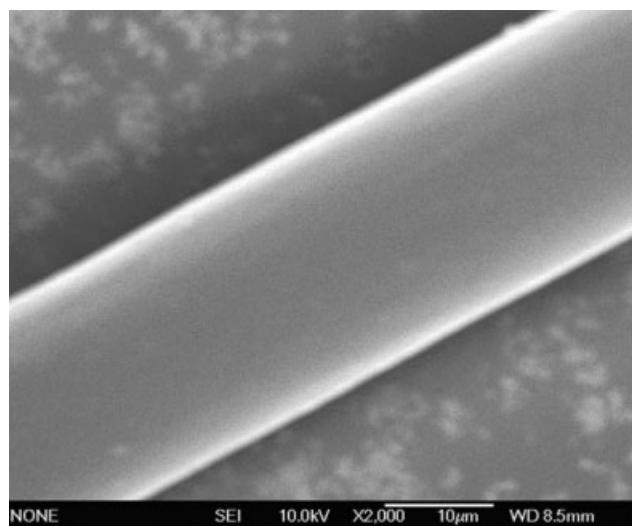
Figure 1 The antibacterial rate of antibacterial PET samples in different times.



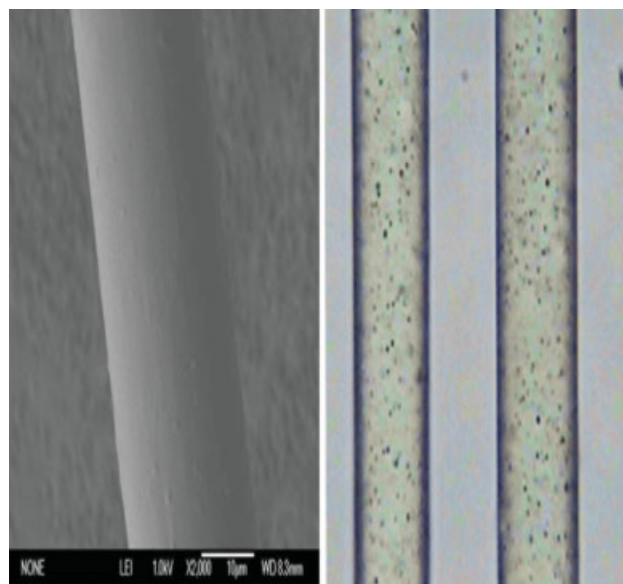
**Figure 2** SEM micrograph of antibacterial masterbatch.

micrograph (Fig. 2), black area is PET matrix and white parts are antibacterial materials. The SEM micrograph demonstrates that antibacterial materials are well dispersed in the polymer matrix with less large aggregation.

The microstructure of pure PET fibers was observed by SEM (Fig. 3). The surface of pure PET fibers looks very satiny in appearance and has a diameter of about 25 µm. Figure 4 is the SEM and optical micrographs of the antibacterial PET fibers in which 5% antibacterial masterbatch were added. In Figure 4(a), many little particles can be found, which were well embedded within the polymer matrix, and these particles were relatively homogeneous, despite very little agglomerations could be found. The phenomena were also found in the optical micrograph [Fig. 4(b)].



**Figure 3** SEM micrograph of pure PET fibers.

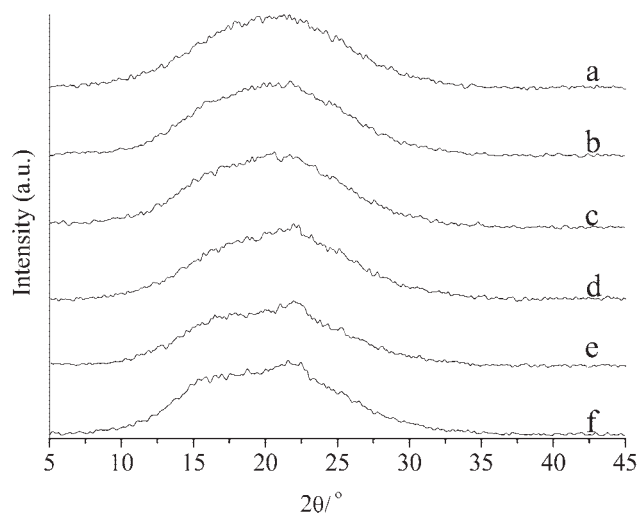


**Figure 4** SEM and optical micrographs of antibacterial PET fibers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

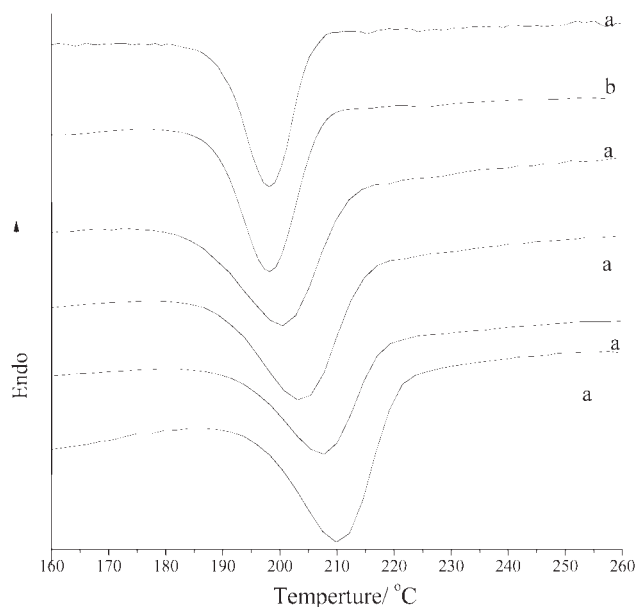
#### Microstructure of antibacterial PET fibers

X-ray diffractograms of PET and composite antibacterial PET fibers are presented in Figure 5. As shown in Figure 5, pure PET fibers and antibacterial fibers having 1.5 and 3% antibacterial masterbatch have main amorphous regions. When more 5% antibacterial masterbatch was added, little crystalline diffraction peaks at about 15° and 22°, which correspond to the (100) and (010) lattice plane of PET fibers,<sup>12</sup> were found in the X-ray diffractograms; although the main structure are amorphous.

These results were further explored by the DSC cooling curves of PET and composite antibacterial



**Figure 5** XRD patterns of PET and composite antibacterial PET fibers: weight concentration of antibacterial materials: (a) 0%, (b) 1.5%, (c) 3%, (d) 5%, (e) 7%, and (f) 9%.



**Figure 6** DSC cooling crystallization curve of PET and composite antibacterial PET fibers: weight concentration of antibacterial materials (a) 0%, (b) 1.5%, (c) 3%, (d) 5%, (e) 7%, and (f) 9%.

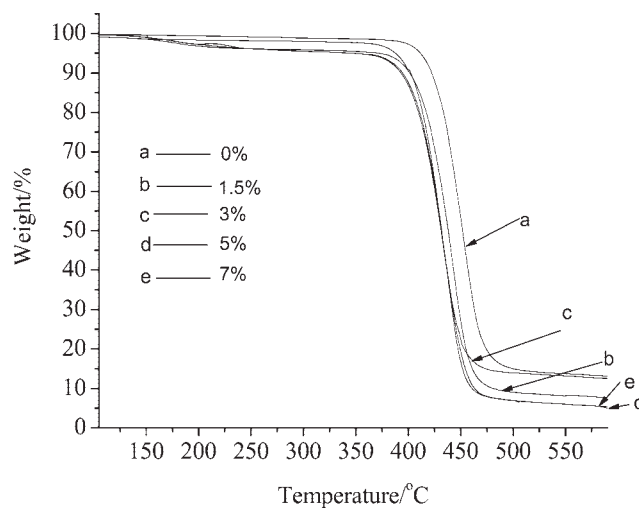
PET fibers, which are shown in Figure 6. By comparing these curves, we found that the cooling crystal temperature ( $T_c$ ) shifted to higher temperature with the increase of content of antibacterial materials. The reason is that the antibacterial materials played a heterogeneous nucleation agent role when the composite antibacterial fibers were cooled. So, the critical temperature was increased.

The orientation is of considerable importance for evaluating the microstructure of fibers. To measure the orientation factor in a polymer, there are a number of different techniques, depending on the constitution. The use of double-refraction methods is of considerable importance for providing information about the degree of orientation in a molecular system.

The effect of the content of antibacterial materials on the double refraction of composite antibacterial

**TABLE II**  
The  $\Delta n$  Value of Composite Antibacterial PET Fibers

Samples	The content of antibacterial materials (%)	Double refraction $\Delta n \times 10^{-2}$
0#	0	2.2
1#	1.5	2.16
2#	3.0	2.07
3#	5	2.0
4#	7	1.9
5#	9	1.7



**Figure 7** Temperature dependences of weight loss for: weight concentration of antibacterial materials: (a) 0%, (b) 1.5%, (c) 3%, (d) 5%, (e) 7%, and (f) 9%.

PET fibers is shown in Table II. Proverbially, the  $\Delta n$  is a positive correlation to break strength and a negative correlation to extensibility. It can be seen from Table II that the  $\Delta n$  decreased with increasing content of antibacterial materials. The phenomenon is associated with the decrease of PET macromolecule arrangement extent along fibers axis because of the antibacterial materials added in the structure. The change of  $\Delta n$  was same with these results of mechanical properties, that is, the break strength of the composite antibacterial fibers was decreased, but the extensibility increased with increasing content of antibacterial materials.

#### Thermal stability of composite antibacterial PET fibers

The thermogravimetric curves are plotted in Figure 7. The degradation of pure PET began at about 400°C, and the maximum decomposition rate appeared at about 450°C. After the antibacterial materials containing coupling agents were added, the onset degradation temperature ( $T_o$ ) of the composite PET system was lowered because of the coupling agent degradation. Compared with the pure PET, there were two thermal degradation stages for the systems containing antibacterial materials. One degradation stage was for the coupling agent in antibacterial masterbatch added, and the other was for the PET. The fastest decomposition temperature ( $T_d$ ) for the first stage appeared at 200°C. The  $T_d$  of the composite antibacterial PET fibers for the second stage appeared at almost the same level as the pure PET. The antibacterial materials have less influence on the thermal degradation of the composites, but the residue weight of the composite antibacterial fibers was

**TABLE III**  
**Comparison Between Aged Property and Bactericidal**  
**Actions of Antibacterial PET Before and**  
**After Aging Treatment**

The aged time (h)	Break-down strength (cN/dtex)		Antibacterial rate (%)	
	Antibacterial fibers	Virgin fibers	<i>S. aureus</i>	<i>E. coli</i>
5	1.96	2.07	96	90
10	1.91	1.96	95	89
15	1.88	1.92	92	85
25	1.84	1.85	93	85
40	1.81	1.80	92	86

decreased, the possible reason is that the adding of antibacterial materials accelerated the degradation of PET.

#### Aged properties of the composite antibacterial PET fibers

Table III shows tensile strengths and antibacterial properties of antibacterial PET fibers (5% antibacterial masterbatch) and virgin fibers subjected to artificial accelerated aging for different exposure time.

The tensile strength of unaged virgin PET fibers and antibacterial fibers are 2.09 and 1.98 cN/dtex, respectively. After UV irradiation, 10 h, the tensile strength of average virgin PET fibers dropped from 2.09 to 1.96 cN/dtex and the tensile strength of antibacterial PET fibers dropped from 1.96 to 1.91 cN/dtex. Exposure continued for another 30 h, during which the average virgin fibers' tensile strength dropped from 1.96 to 1.80 cN/dtex and dropped from 1.91 to 1.81 cN/dtex for the antibacterial fibers. The results demonstrated that the loss rate of tensile strength appears to be near linear with exposure time. However, the loss rate of tensile strength of antibacterial PET fibers is slower than the virgin PET fibers.

The effect of the aging time on the antibacterial activity of antibacterial fibers against *S. aureus* and *E. coli* are also shown in Table III. The results showed that the antibacterial activity of the antibacterial fibers slightly decreased with the aging time, after 24 h of aging, the antibacterial rate against *S. aureus* and *E. coli* are 92 and 86%, respectively, which still meets the State Standard GB1598-1995. Hence, the antibacterial activity of antibacterial fibers was unaffected by the artificially accelerated aging.

## CONCLUSIONS

In this study, antibacterial composite PET fibers were made by melt compounding and high-speed melt-spinning. The influence of contents of antibacterial materials on the antibacterial properties, mechanism properties, microstructures, crystallization behavior, and thermal stability of antibacterial composite PET fibers were investigated.

Without antibacterial materials, the pure PET fibers had a little higher break strength, but had lower tensibility than the antibacterial composite PET fibers. The extensibility and antibacterial ratios of antibacterial composites had maxima with antibacterial materials content at 5%, except the break strength had little decrease.

The SEM micrograph of antibacterial composite PET fibers demonstrated that the antibacterial materials were well dispersed in the polymer matrix with little large aggregation. So, the mechanical property of fibers was still better.

X-ray diffractograms and DSC curves of PET and composite antibacterial PET fibers suggested that the antibacterial materials as a heterogenous nucleation agent accelerated the crystallization of PET. However, the  $\Delta n$  decreased with increasing content of antibacterial materials.

There were two thermal degradation stages for the antibacterial composite PET fibers. The first, appearing at a much lower temperature was for coupling agents, and the second was for the PET. The antibacterial materials had little influence on the thermal degradation of the composites.

The loss rate of tensile strength of aged fibers appears to be near linear with exposure time. However, the loss rate of tensile strength of antibacterial PET fibers is slower than virgin PET fibers.

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