Preparation and Properties of a New Coating Method for Preparing Conductive Polyester Fibers with Permanent Conductivity

Xin Jin, Changfa Xiao, Shulin An, Yongyue Wang, Guangxia Jia

Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber (FMFF), Tianjin Polytechnic University, Tianjin, 300160, China

Received 22 July 2005; accepted 27 December 2005
DOI 10.1002/app.24095
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new coating method based on dissolution (the dissolving-coating method) was designed to prepare carbon black–coated electrically conductive polyester fibers. The effects of the composition of the coating mixture on the volume resistivity of the fibers were investigated. The mechanical properties and conductive permanence of the coated fibers were studied. The coated fibers prepared by the dissolving-coating method had the characteristics of lower volume resistivity (9.6×10^0 Ω cm) and permanent conductivity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2685–2691, 2006

Key words: polyesters; modification; coatings; fibers; surfaces

INTRODUCTION

Although poly(ethylene terephthalate) (polyester) fibers are used in a great many textile and industrial materials, their undesirable hydrophobic and electrical insulating properties inevitably bring about disadvantages such as the accumulation of static charge under dry conditions, which is not only harmful to the human body, but is also dangerous in some situations.[1,2]

To remedy these problems, a number of studies have focused on how to impart conductivity to polyester fibers. Currently, many researchers are investigating melt spinning technology. In this method, conductive fibers are prepared through the blending of nanoparticles (carbon black or metal) with polyester melt. The nanoparticles are well dispersed in the polymer matrix and become a part of the structure of the fibers.[3–5] This characteristic imparts permanent conductivity to the fibers. But to obtain lower volume resistivity, a higher concentration of nanoparticles is often required, resulting in bad spinnability and a decrease in the mechanical properties of the final fibers.[6–8]

Post-treatment is another method for preparing electrically conductive polyester fibers, which is achieved by a coating with nanoparticles[9–12] or deposition of intrinsically conducting polymers (ICPs) on the surface of polyester fibers.[13,14] This kind of method is less costly and easier to operate than the melt-spinning technology. With the coating method, the nanoparticles placed on the outside of the fibers contribute strongly to imparting conductivity to the polyester fibers. Therefore, compared with melt-spinning technology, the coating method can impart lower volume resistivity to conductive polyester fibers. However, the nanoparticles adhere to the fiber surface because of adhesive,[9–12] and it is impossible for them to become a part of the fiber structure. This disadvantage results in coatings on the surface of fibers lacking cohesion and decreased permanence of conductivity with each additional washing cycle.[6,15,16] Economy and lower volume resistivity are achieved only through sacrifices in the permanence of the conductivity of the fibers.

Therefore, it is desirable to explore a new type of coating method, one that would possess not only the advantages of the traditional coating method, but also the advantages of melt-spinning technology. This new kind of coating method would make possible electrically conductive polyester fibers that are lower in cost and volume resistivity, yet durable. To achieve this, the new type of conductive polyester fiber would have to have unique properties:

1. The nanoparticles should be distributed on the surface of fiber, ensuring that the coated fibers have lower volume resistivity.
2. The nanoparticles should become a part of the structure of the fiber in order to achieve permanent conductivity.
3. The excellent mechanical properties of the fiber substrate should not be adversely affected.

Correspondence to: C. Xiao (cfxiao@tjpu.edu.cn).

© 2006 Wiley Periodicals, Inc.

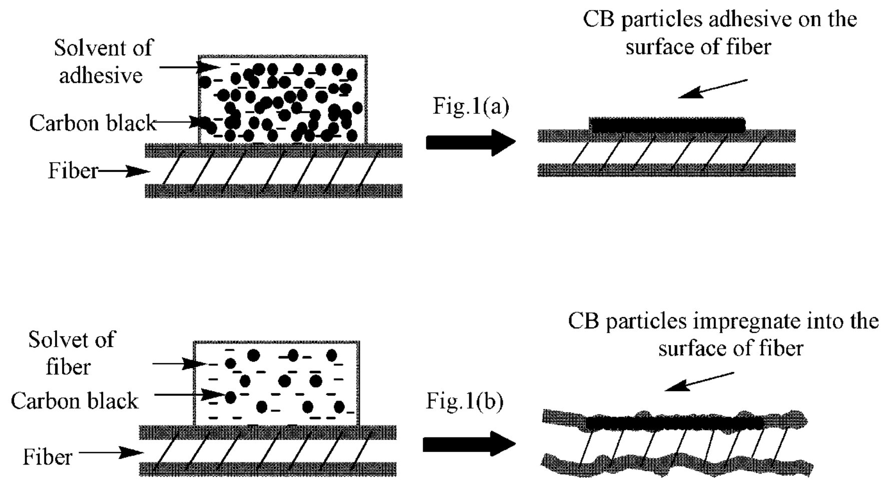

Figure 1 Schematic progress of coating method: (a) traditional coating method and (b) dissolving-coating method.

In this article we report the development of such a new coating method for preparing electrically conductive polyester fibers. With this new coating method, a true solvent of the fiber substrate is chosen in which carbon black (CB) is dispersed. When there is true dissolution of the fiber surface, the surface of the fiber can be uniformly suffused with the CB in the solvent, and CB becomes part of the structure of the fiber. We have termed this new coating method the dissolving-coating method. Figure 1 schematically illustrates the processes of both the traditional coating method and the dissolving-coating method. The present study investigated the effects of the coating mixture on the electrical properties. The mechanical properties and conductive permanence were also studied.

EXPERIMENTAL

Materials

Electrically conductive CB, used as the conductive particles, obtained from the Huaguang Chemical Factory (Zibo City, China). The average primary CB particle was 29 nm in diameter, and DBP was 380 mL/100 g. Monofilaments of poly(ethylene terephthalate) (polyester, 80 denier) were supplied by the Ruisheng Fiber Company (Wuxi City, China). Other reagents in the research were supplied by Tianjin Chemical Reagent Institute.

Preparation of CB-coated polyester fibers

CB particles were treated by a titanate coupling agent, which was sprayed on CB under high-speed stirring while being heated to react for certain time. In the dissolving-coating method, the coating mixture was prepared by dispersing the treated CB particles in a 50 : 50 phenol/tetrachloroethane solution using a ball mill. Then the coating mixture was coated to the polyester fiber substrates on the coating machine shown in Figure 2, which was designed in our laboratory. The coating machine had a grooved roll-type coating applicator for uniformly applying the coating mixture to the fiber surface. An evaporation tube was used to immediately remove the solvent. Then the coated fibers were washed in an ultrasonic bath in order to eliminate any solvent remaining on the surface of the fibers. All the coated fibers were prepared with the

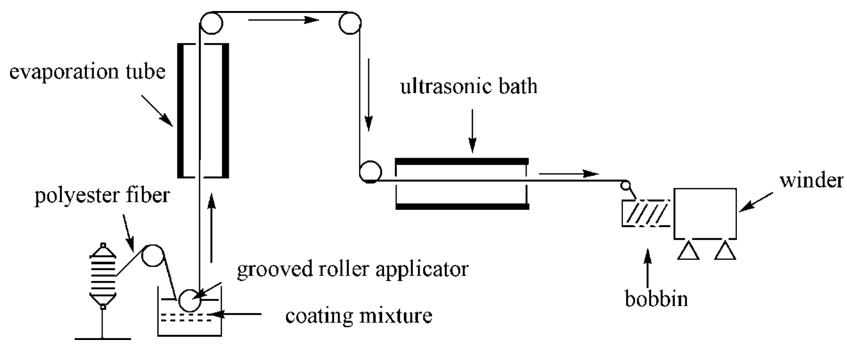

Figure 2 Fiber-coating machine used in this study.

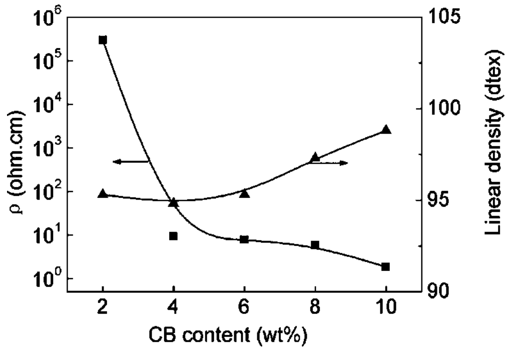

Figure 3 Effect of CB content on volume resistivity and linear density of fiber.

same coating time and winding speed. In addition, to increase the viscosity of the coating mixture, we designed a coating mixture containing the same dissolved polymer as that of the fiber substrate.

To test the conductive durability of the CB-coated polyester fibers prepared by the dissolving-coating method (designated ECF1), the CB-coated polyester fibers were also prepared by the traditional coating method (designated ECF2). In the traditional coating method, polyurethane (PU) was used as the adhesive and was dissolved in dimethylformamide (DMF) at a ratio of 1 : 4 (w/w). The treated CB particles were dispersed in these PU-DMF solutions to prepare the coating mixture. Then the coating mixture was coated on the polyester fibers substrate.

Preparation of plain woven fabric

Plain-woven fabrics containing coated ECF1 and ECF2 were made. The base fabric was polyester, and the electrically conductive fibers (ECFs) formed a striped pattern in the fabric. The interval between the ECFs in the base fabric was always maintained at 2.5 cm in the warp direction.

Characterization

The electrical resistance, R (ohm), of the fibers was measured with a two-lead system at room temperature. Volume resistivity, ρ (Ω cm), was calculated using the following equation: $\rho = RA/L$, where A and L are the area and the length, respectively, of the tested fiber.

The mechanical properties of the fibers were measured with a tensile test machine (PC/LLY-06, Laizhou Electron Instrument, China) at a drawing speed of 20 mm/min. Five specimens from each sample were tested, from which an average was calculated.

The structure of the fibers was examined by dynamic mechanical analysis (DMA; Perkin–Elmer; 1 Hz, 5°C/min) and scanning electron microscopy (SEM).

The two types of fabrics, one containing ECF1 and the containing ECF2 were washed in a commercial washing machine with a commercial washing powder under the same conditions. Laundering cycle was varied, and each laundering time was 5 min. Then the surface-charge density of the fabrics with different laundering cycles was measured. Before testing, the fabrics were conditioned at 12% ± 3% relative humidity at 22°C ± 2°C for 72 h. Then the surface-charge density ($\mu C/m^2$) of the fabrics was measured in the direction of warp under the same conditions (charge instrument, model EST111, Beijing Institute, China). Each measurement was repeated five times.

RESULTS AND DISCUSSION

Preparation

Effect of CB content in the coating mixture

The composition of the coating mixture was one of the most important factors affecting the volume resistance of the CB-coated polyester fibers. Figure 3 shows the volume resistivity and linear density of the fibers as a function of CB content in the coating mixture. Apparently, the volume resistivity changed by many orders of magnitude when the CB content was at the critical content (4 wt %). That is, when CB content was less than the critical content, volume resistivity was high, which decreased dramatically when CB content came close to the critical content. But when CB content was greater than the critical content, there was less variation in volume resistivity with CB content. This sudden jump in volume resistivity was attributed to the formation of the first ''infinite'' agglomerate pathway, which allowed electrons to travel a macroscopic distance through the coated fiber. Meanwhile, the linear density of the coated fiber did not change much with increasing CB content.

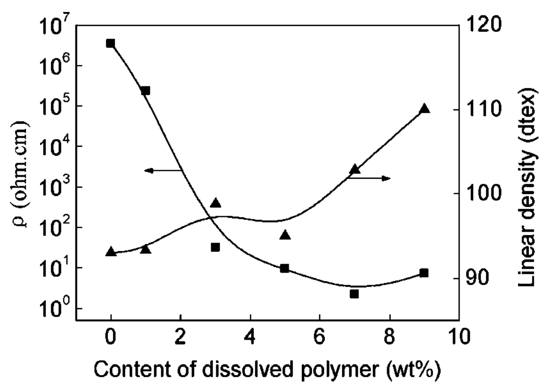

Figure 4 Effect of dissolved polymer content on volume resistivity and linear density of fiber (CB content was 4 wt %).

TABLE I
Properties of Original Fibers and Coated Fibers (ECF1 and ECF2)

Samples	Volume resistivity (Ω cm)	Linear density of fiber (*dtex*)	Mechanical properties: Tenacity at break, *F*(*cN*/*dtex*)	Elongation at break, *E* (%)	Work at break, *W* (mJ)	Time at break, *T* (s)
Original fiber	$> 10^{13}$	89.6	4.20	11.32	72.2	33.25
Coated ECF1	9.6×10^{0}	95.0	3.85	10.58	67.8	27.55
Coated ECF2	1.86×10^{1}	100.0	4.20	12.17	70.8	32.62

Effect of dissolved polymer content in the coating mixture

At a given CB content in the coating mixture, volume resistivity was affected by the content of dissolved polymer in the coating mixture. The volume resistivity and linear density of the coated fibers were plotted against the dissolved polymer content, shown in Figure 4. Volume resistivity decreased with an increasing dissolved polymer content of the coating mixture, reaching a plateau when the dissolved polymer content was greater than 5 wt %. And the linear density of the fibers dramatically increased when the dissolved polymer content was greater than 5 wt %. The reason we designed a coating mixture that contained dissolved polymer of the same fiber substrate was to increase the viscosity of the coating mixture. Having a coating mixture of the desired viscosity can make CB disperse more uniformly and can make the coating mixture cling to the fiber surface after application. Thus, during application of the coating mixture to the fiber surface, not only was the area in contact with the grooved roller coating applicator exposed to the coating, but also the area between the coating applicator and the evaporation tube. That is, the relative coating time increased. This resulted in the diffusion and dissolution being carried through fully. More CB particles would suffuse the fiber surface, and a continuous network would easily form on the fiber surface in the same coating time. Therefore, when the dissolved polymer content reached 5 wt %, the volume resistivity of the coated ECF1 decreased dramatically by several magnitudes to 9.6×10^{0} Ω cm. But when the dissolved polymer content increased to 9 wt %, the coating mixture become too viscous. This did not benefit volume resistivity but resulted in the linear density of the coated fibers increasing a lot and the surface becoming rough.

Properties

Electrical and mechanical properties

Using the dissolving-coating method, the dissolution of the fibers might lead to a decrease in the mechanical properties of the final fibers. For the dissolving-coating method to have utility, the solvent of the fiber substrate must be removed before the structural integ-

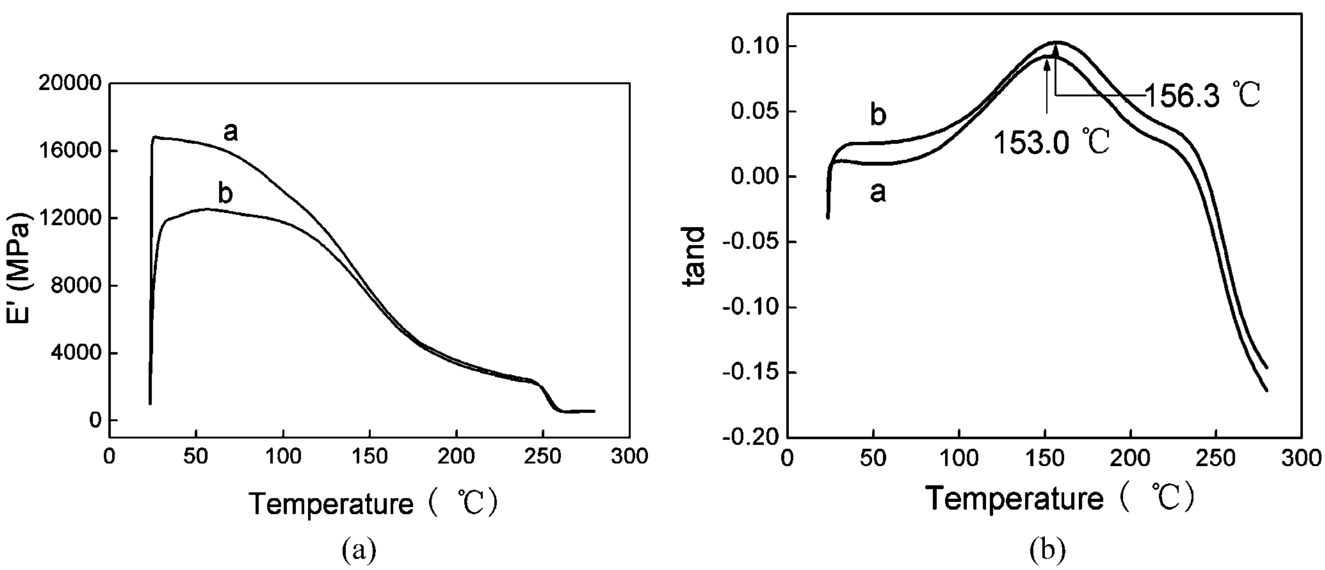

Figure 5 DMA analysis of (a) original fiber substrate and (b) coated ECF1.

TABLE II
Washing Test of the Two Kinds of Fabrics

Fabrics	Surface-charge density of fabrics with different laundering times (μC/m²)			
	Before washing	10 washing cycles	50 washing cycles	100 washing cycles
Containing ECF1	4.1	3.1	3.4	4.1
Containing ECF2	5.2	5.0	8.6	9.8

The ECF formed stripes in the warp direction, and the intervals of the ECF were constant at 2.5 cm.

rity of the fiber. This is the premise of the dissolving-coating method. The evaporation tube of the coating machine can remove the solvent immediately after application. Table I shows the electrical and mechanical properties of the original fiber substrate and the coated ECF1 and ECF2. It can be seen from Table I that the dissolving-coating method can provide fibers with lower volume resistivity and smaller linear density than those of the traditional coating method. Meanwhile, the mechanical properties data, shown in Table I, indicating that the dissolving-coating method can impart higher conductivity to polyester fibers without adversely affecting the excellent mechanical properties of the fiber substrate.

To test the mechanical properties of ECF1 further, DMA analysis of the fiber substrate and ECF1 was also carried out. The storage modulus, E', and loss tangent, tan δ, of the original fiber substrate and ECF1 are shown in Figure 5, from which it can be seen that, compared to the original fiber substrate, the E' of the coated ECF1 decreased a little and the peak of tan δ moved to a slightly higher temperature. These results confirmed that the dissolving-coating method has the advantage of creating conductive polyester fibers without impairing the mechanical properties of the original polyester fibers.

Permanence of conductivity

Two types of plain-woven fabrics, one containing ECF1 and the other containing ECF2, were prepared to have the same pattern. The permanence of conductivity of the CB-coated polyester fibers was tested through washing with water. These fabrics were subjected to different washing cycles under the same conditions. The results for the surface-charge density of the fabrics with different washing cycles are listed in Table II. It can be seen that both the traditional coating method and the dissolving-coating method can produce fabrics with a satisfactory surface-charge density before washing. With an increasing number of washing cycles, the fabric containing ECF1 remained stable throughout the washing test. However, the surface-charge density of the fabric containing ECF2 increased dramatically after 100 washing cycles.

SEM micrographs of the fiber are shown in Figure 6. It can be clearly seen from Figure 6(a) that the surface of the original polyester fiber was smooth. Figure 6(b) shows some irregular marks after the original fiber was dipped in the solvent, which should be attributed to the surface layer being dissolved by the solvent. Before being washed, the surfaces of both ECF1 and ECF2 samples were uniformly coated with CB particles, which can be observed in Figure 6(c). After 100 washing cycles, the coating of ECF1 was not abraded and incoherent, as shown in Figure 6(e). However, the coating of ECF2 partly flaked because of the abrasion and washing displayed in Figure 6(f). For ECF1 made by the dissolving-coating method, CB was impregnated in the surface of the fiber layer and had already become part of the structure of the fiber. So the coating would not be destroyed with a large number of washing cycles. But for ECF2, the CB adhered to the fiber surface because of adhesive, which resulted in the coating being abraded, incoherent, and even flaking due to washing. Therefore, the washing test and SEM photographs confirmed that the ECF1 made by the dissolving-coating method had permanent conductivity.

CONCLUSIONS

This article has introduced the dissolving-coating method, a new coating method that differs from the traditional coating method. The effects of the coating mixture on the electrical properties of the coated fibers were discussed, as were the mechanical properties and conductive permanence of the coated fibers. The results showed that the volume resistivity of the fibers studied could reach $9.6 \times 10^0\ \Omega$ cm when the CB content of the coating mixture was 4 wt %. The desirable characteristics of the fiber polymer substrate were retained while at the same time achieving significant conductivity. The washing test and SEM photographs confirmed that the fibers prepared by the dissolving-coating method had permanent conductivity unlike the coated fibers prepared

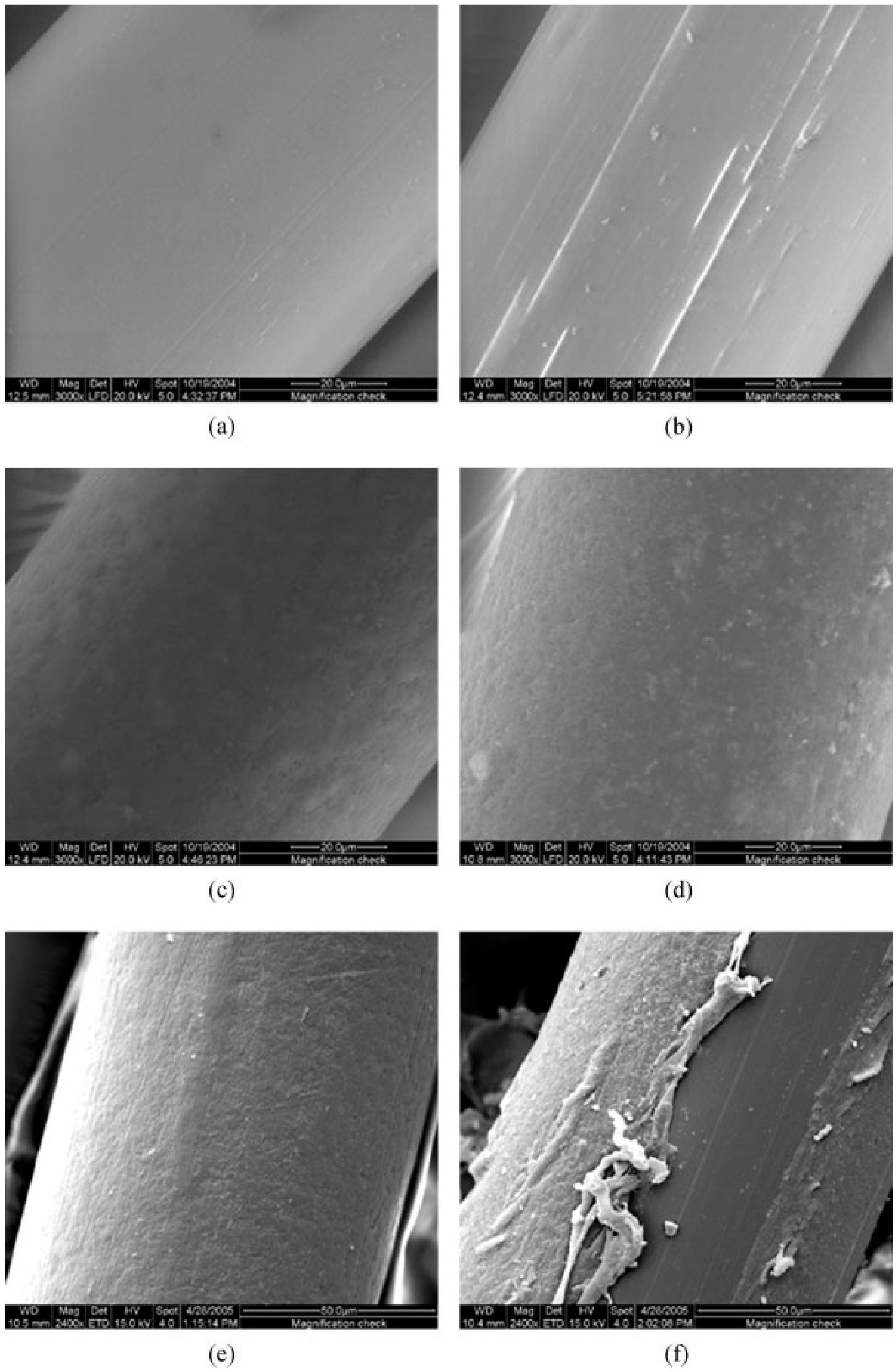

Figure 6 Surface SEM photographs of fibers: (a) original PET fiber, (b) original PET fiber dipped in solvent, (c) ECF1, (d) ECF2, (e) ECF1 after 100 washing cycles, (f) ECF2 after 100 washing cycles.

by the traditional coating method. So the dissolving-coating method is an effective way to provide CB-coated polyester fibers with the characteristics of lower volume resistivity, conductive permanence, and easy operation.

References

1. Kim, M. S.; Kim, H. K.; Byun, S. W.; Jeong, S. H.; Hong, Y. K.; Joo, J. S.; Song, K. T.; Kim, J. K.; Lee, C. J.; Lee, J. Y. Synth Met 2002, 126, 233.
2. Kaynak, A.; Beltran, R. Polym Int 2003, 52, 1021.

3. Kim, D. J.; Seo, K. H.; Hong, K. H.; Kim, S. Y. Polym Eng Sci 1999, 39, 500.
4. Pomfret, S. J.; Adams, P. N.; Comfort, N. P.; Monkman, A. P. Synth Met 1999, 101, 724.
5. Kim, B.; Koncar, V.; Devaux, E.; Dufour, C.; Viallier, P. Synth Met 2004, 146, 167.
6. Wang, D.; Lin, Y.; Zhao, Y.; Gu, L. Text Res J 2004, 74, 1060.
7. Zhang, Q. H.; Chen, D. J. J Mater Sci 2004, 39, 1751.
8. Mallette, J. G.; Quej, L. Q.; Marquez, A.; Manero, O. J Appl Polym Sci 2001, 81, 562.
9. Cilffi, N.; Torsi, L.; Sabbatini, L.; Zambonin, P. G.; Bleve-Zacheo, T. J Elec Chem 2000, 488, 42.
10. Huang, C. Y.; Wu, C. C. Eur Polym J 2000, 36, 2729.
11. Boe, N. W. U.S. Pat. 4,129,677 (1978).
12. Ellis, V. S.; Mieszkis, K. W. U.S. Pat. 4,388,370 (1983).
13. Wha, K.; Kim, S. H.; Kim, E. A. J Appl Polym Sci 2001, 81, 684.
14. Hirase, R.; Hasegawa, M.; Shirai, M. J Appl Polym Sci 2003, 87, 1073.
15. Yee, T. B. U.S. Pat. 4,247,596 (1981).
16. Asher, P. P.; Lilly, R. L.; Davenport, G. L.; Hyatt, R. K.; Rogers, C. H. U.S. Pat. 5,952,099 (1998).