Surface Nanostructures and Dynamic Contact Angles of Functionalized Poly(ethylene terephthalate) Fibers

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ABSTRACT: An approach (a combination of techniques) to studying poly(ethylene terephthalate) (PET) fibers metal-coated by the sputtering of copper is reported. The effects of copper coatings on the surface morphology, surface chemistry, and surface energy were investigated with atomic force microscopy (AFM), energy-dispersive X-ray (EDX) analysis, and dynamic contact angle measurements. Functional nanostructures formed by sputter coating on the fiber surface were revealed with AFM. The introduction of copper onto the fiber surface was also detected by EDX analysis. The fibers functionalized by the sputter coating resulted in changes in the surface energy measured with the advancing and receding contact angles. Both the advancing and receding contact angles were reduced after sputter coating by copper, but the contact angle hysteresis was significantly increased as the coating was applied. The surface resistivity measurements revealed that sputter coating by copper considerably improved the surface conductivity of the PET fibers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109:654–658, 2008

Key words: atomic force microscopy (AFM); coatings; fibers; morphology; surfaces

INTRODUCTION

Various types of fibers have been widely used to manufacture textile materials for a variety of applications. Natural fibers had dominated the textile market for thousands of years, but new developments in the synthetic fiber industry have significantly changed the textile industries.[1] The use of various synthetic fibers has been expanding from modern apparel and home furnishings to medicine, aeronautics, the energy industry, and other areas of technical applications. The synthetic fibers used in different forms of technical textiles include olefin fibers, poly (ethylene terephthalate) (PET) fiber, and rayon fibers.[2]

PET fiber has become one of the most important materials in various industries because of its inherent characteristics, such as superior strength and resilience. For the expanding applications of PET fibers, it is also desirable to produce such fibers with well-defined surface structures and properties. Various techniques, such as physical vapor deposition, electroless deposition, and sol–gel deposition, have been employed to modify the surface properties of textile materials.[3–5] Among all of these, sputter coating[6] has proven to be one of the most promising techniques for the functionalization of textile materials. Sputter-coating technology has advantages such as a uniform coating and compact structures, strong bonding between the film and its substrate, and environmentally friendly techniques.[7] Sputter coating has also been used to functionalize textiles.[8,9] A better understanding of the effect of sputter coating on the surface structures and properties will lead to the development of new functional textiles for different applications.

In this study, PET fibers were functionalized through the sputter coating of copper (Cu). The effects of the Cu coatings on the surface morphology, surface chemistry, and surface energy were investigated with atomic force microscopy (AFM), energy-dispersive X-ray (EDX) analysis, and dynamic contact angle measurements. The effect of Cu sputter coating on the surface conductivity was also investigated.

EXPERIMENTAL

Materials

Fibers used in this study were PET fibers obtained from Changzhou Huayuan (Changzhou, China). The

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PET fibers had an average diameter of 28 μm. The fiber samples were first washed in ethanol (Sinopharm Chemical Reagent Co. Ltd., Shenyang, China), and this was followed by two rinses in distilled water; then, they were dried at 40°C in an oven.

Sputter coating

Sputter coating by Cu was performed in a magnetron sputter coating system (Shenyang Juzhi Co., Ltd., Shenyang, China). The metallic coatings of Cu were deposited onto the surface of PET fibers at room temperature. High-purity Cu targets (diameter = 50 mm, purity = 99.999%; MTI Corp., Hefei, China) were used in this work. The fibers were hung onto the sample holder by one end of the fibers being fixed to the sample holder. The sample holder (the substrate holder) was kept rotating at a speed of 100 rpm to ensure a uniform coating on the surface of the fiber during the sputtering. The sputter chamber was first pumped to a base pressure of 5×10^{-4} Pa before the introduction of high-purity argon gas (99.999%) as a bombardment gas. The thickness of the coating was monitored with an FTM-V coating thickness detector (Shanghai Tairao Vacuum Technology Co., Ltd., Shanghai, China) fixed in the sputtering chamber. The coating was performed at a pressure of 0.8 Pa with a power of 60 W. The thickness of the prepared coatings was 20, 50, or 100 nm.

Surface morphology

The surface morphologies of the fibers before and after the coating were examined with a CSPM4000 scanning probe microscope (Benuyuan Co., Ltd., Guangzhou, China). Scanning was performed with contact-mode AFM at room temperature under an air atmosphere. A CSC11 silicon probe (MikroMasch, San Jose, CA) was used. The radius of curvature was less than 10 nm, and the spring constant was 0.35 N/m. The scanning size was 5000 nm × 5000 nm, and the scanning frequency was set at 1.0 Hz.

EDX analysis

An XL30 environmental scanning electron microscope (Fei, Hillsboro, OR) integrated with a Phoenix (Mahwah, NJ) EDX detector was used to scan the surface of the fiber. The charging artifacts were eliminated to ensure the presence of gas (usually water vapor) in the sample chamber of the environmental scanning electron microscope.[10] This experimental setup allowed analyzing the elemental compositions down to boron, including light elements such as carbon, nitrogen, and oxygen, but hydrogen could not be detected in this EDX analysis. In this study, the fiber surface was examined by EDX analysis at an accelerating voltage of 20 kV with an accounting time of 100 s. A size of about 10 μm × 10 μm was selected for the PET fiber for EDX analysis in the environmental scanning electron microscope.

Electrical conductivity

The electrical properties of the fibers were examined by resistivity measurements with a collinear four-probe array (SX1934, Baishen Technologies, Suzhou, China). To minimize the deviations brought by the unevenness of the fiber surface, the resistivity of each sample was measured three times, and the average values were used.

Dynamic contact angles

The dynamic wetting behavior of the fibers was investigated by dynamic contact angle measurements of individual fibers. The measurement of the dynamic contact angles was performed on a CDCA-100F (Camtel, Ltd., Royston, UK). The dynamic contact angles were determined by the Wilhelmy technique:[11] a solid sample was immersed and withdrawn into and out of a liquid while the force acting on the solid sample was simultaneously measured at 20°C. The advancing and receding contact angles could then be obtained from the measured force curve. Distilled water was used for the dynamic contact angle measurements.

RESULTS AND DISCUSSION

Surface morphology

An AFM image reveals the surface morphology of the original PET fiber, as shown in Figure 1(a). It clearly shows that the PET fiber has a relatively smooth surface with some groovelike structures. These structures are probably formed during the process of fiber spinning, which leads to the formation of the tiny grooves along the fiber axis.

Sputter coating by Cu significantly alters the surface characteristics of the PET fibers, as revealed in Figure 1(b–d). During sputtering, energized gas ions strike the Cu target and cause Cu atoms from this target to be ejected with enough energy to travel to and bond with the PET substrate, forming the functional coating. The Cu clusters scatter on the PET fiber surface after coating with a thickness of 20 nm. The Cu clusters have variable sizes ranging from less than 10 nm to over 20 nm, as illustrated in Figure 1(b). As the coating thickness is increased to 50 nm, the Cu clusters coated on the PET fiber surface look more even, and the sizes of the sputtered Cu clusters appear larger, as revealed in Figure 1(c). This is attributed to the collision of the sputtered Cu

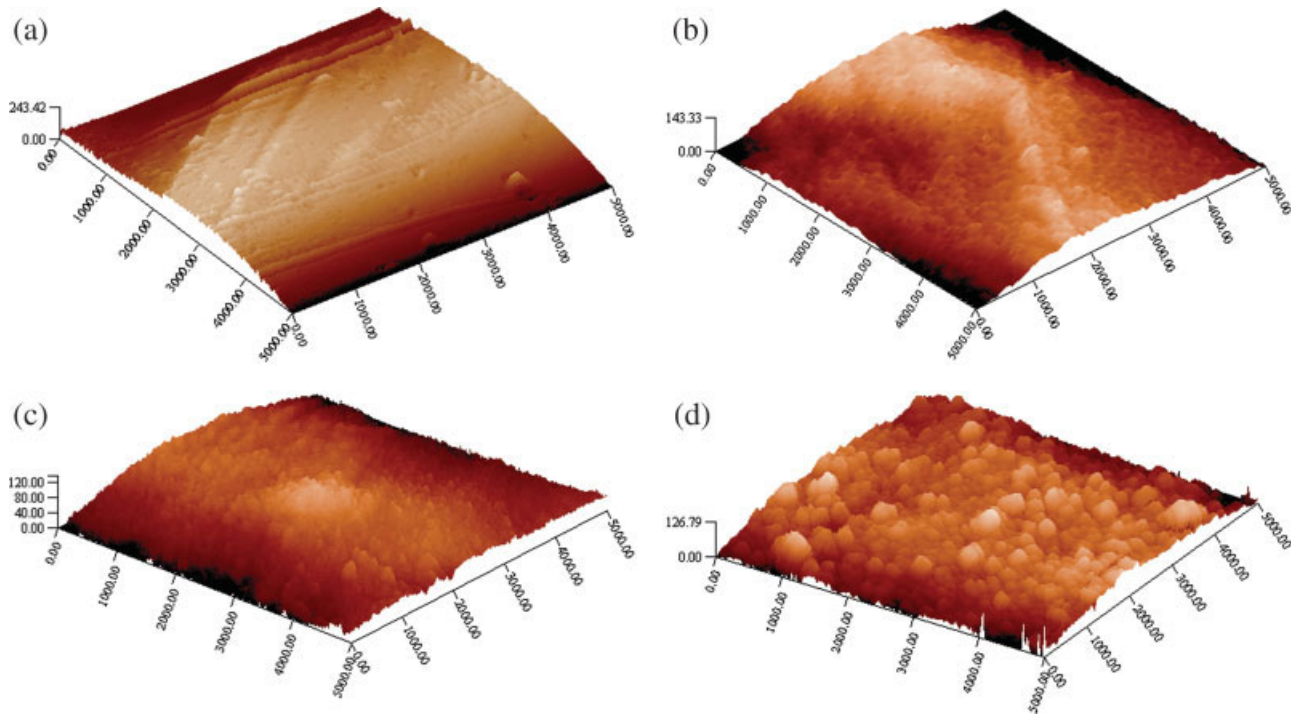

Figure 1 AFM images of (a) the original PET fiber and the fiber with (b) 20-, (c) 50-, or (d) 100-nm coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

grains. The increase in the sputter-coating thickness leads to the growth of the Cu clusters and more compact deposition. The obvious growth of the Cu grains formed on the PET fibers is also observed when the coating thickness is increased to 100 nm, as indicated in Figure 1(d).

The AFM observation also reveals the change in the surface roughness altered by the sputter coating by Cu, as indicated in Table I. The surface roughness of the PET fiber is about 3.67 nm. The surface roughness is increased to 8.08 nm as the Cu coating reaches 20 nm. A further increase in the surface roughness is observed as the coating thickness is increased to 50 nm. The surface roughness is significantly increased to 18.35 nm as the coating is increased to 100 nm. The increase in surface roughness is attributed to the growth of the Cu clusters formed on the PET fiber surface, as revealed in Figure 1.

TABLE I
Surface Structures and Properties

Property	PET	Cu-coated PET		
		20 nm	50 nm	100 nm
Roughness (nm)	3.67	8.08	13.12	18.35
Resistivity (Ω cm)	$>10^6$	43.50	1.27	0.05
Advancing contact angle (°)	85	72	70	70
Receding contact angle (°)	68	50	40	32
Contact angle hysteresis (°)	17	22	30	38

EDX analysis

The chemical components of the functionalized PET fiber surface were examined by EDX analysis. The EDX spectra in Figure 2 show the PET fibers before and after sputter coating by Cu. Figure 2(a) shows that the surface of the PET fibers dominantly consists of carbon and oxygen before the sputter coating by Cu. The chemical composition of hydrogen in the fiber is too light to be detected in this EDX analysis. A significant amount of Cu on the fiber surface after Cu sputter coating with a thickness of 20 nm can be observed from the spectrum, but the amount of carbon and oxygen is reduced in the EDX spectrum; this indicates the coverage of the surface by the Cu coating, as displayed in Figure 2(b). The increase in the coating thickness leads to a decrease of carbon and oxygen and increase of Cu in the spectrum. The EDX spectrum shows no carbon and oxygen detected anymore as the coating thickness reaches 100 nm, indicating the full coverage of the fiber surface by the layer of Cu, as illustrated in Figure 2(c).

Surface conductivity

The surface conductivity of the PET fibers was analyzed with resistivity measurements. The results of

the electrical resistivity measurements for the PET fibers are also listed in Table I. The original PET fiber has a very high surface resistivity greater than 10^6 Ω cm, and this indicates the insulation property of the fiber. The metallic sputter coating by Cu, however, significantly lowers the surface resistance, as revealed in Table I. The surface resistivity of the fiber drops considerably to about 43.5 Ω cm when the coating thickness is only 20 nm. The surface resistivity is further reduced to 1.27 Ω cm as the coating thickness is increased to 50 nm. The surface resistivity is only about 0.05 Ω cm when the coating thickness reaches 100 nm, and this indicates improved surface conductivity.

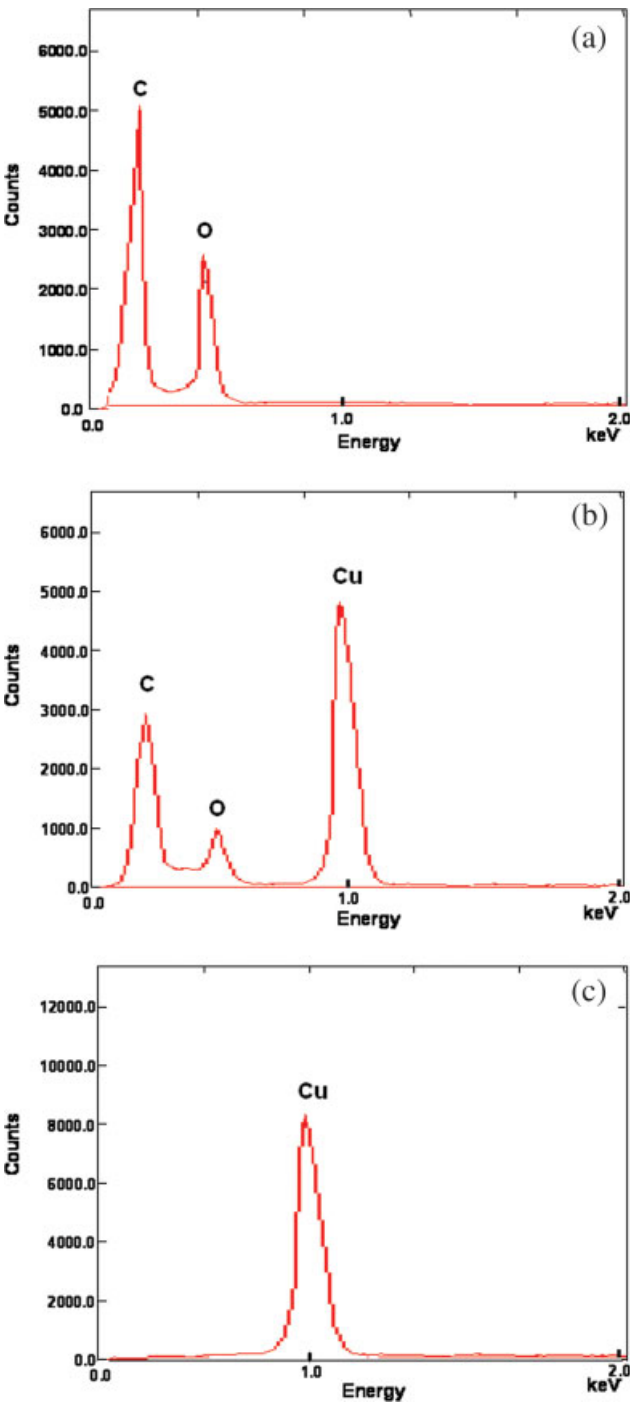

Figure 2 EDX spectra of (a) the original PET fiber and the fiber with (b) 20- or (c) 100-nm coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Dynamic contact angles

The dynamic contact angle measurements reveal the effect of the sputter coating by Cu on the surface wettability of the fibers. Figure 3(a) shows the dynamic contact angles of the original PET fibers, with an average advancing contact angle of about 85° and receding contact angle of about 68°. There is an obvious hysteresis between the advancing contact angle and receding contact angle. The average hysteresis between the advancing contact angle and receding contact angle is about 17°. This hysteresis is attributable to the surface roughness of the PET fiber, as displayed in Figure 1(a).

Figure 3(b) shows the dynamic contact angles of the fiber after sputter coating by Cu with a thickness of 20 nm. Both the advancing and receding contact angles are lowered as the sputter coating is applied. The advancing contact angle is reduced to about 72° from 85°, and the receding contact angle is dropped to 50° from 68°. The decrease in both the advancing and receding contact angles is caused by the surface energy of Cu formed on the PET fiber surface. It has been calculated that the hysteresis is about 22°. The increase in contact angle hysteresis is attributed to the rougher surface caused by the sputter coating of Cu, as shown in Figure 1(b).

The advancing contact angle is about 70° as the coating thickness is increased to 50 nm. The advancing contact angle is very similar to that of the 20-nm-coated fiber, but the receding contact angle drops to 40°, as presented in Figure 3(c). The hysteresis is increased to about 30°. The rougher surface contributes to the increase in the contact angle hysteresis, as illustrated in Figure 1(c). The advancing contact angle does not show much change as the coating thickness is increased to 100 nm, as shown in Figure 3(d). The average advancing contact angle is about 70°. The receding contact angle, however, is further reduced to about 32°, and the contact angle hysteresis is increased to 38°. The prolonged coating seems not to significantly affect the advancing contact angles, but the receding contact angle is considerably influenced.

The effect of the coating thickness on the dynamic contact angle is also listed in Table I for comparison.

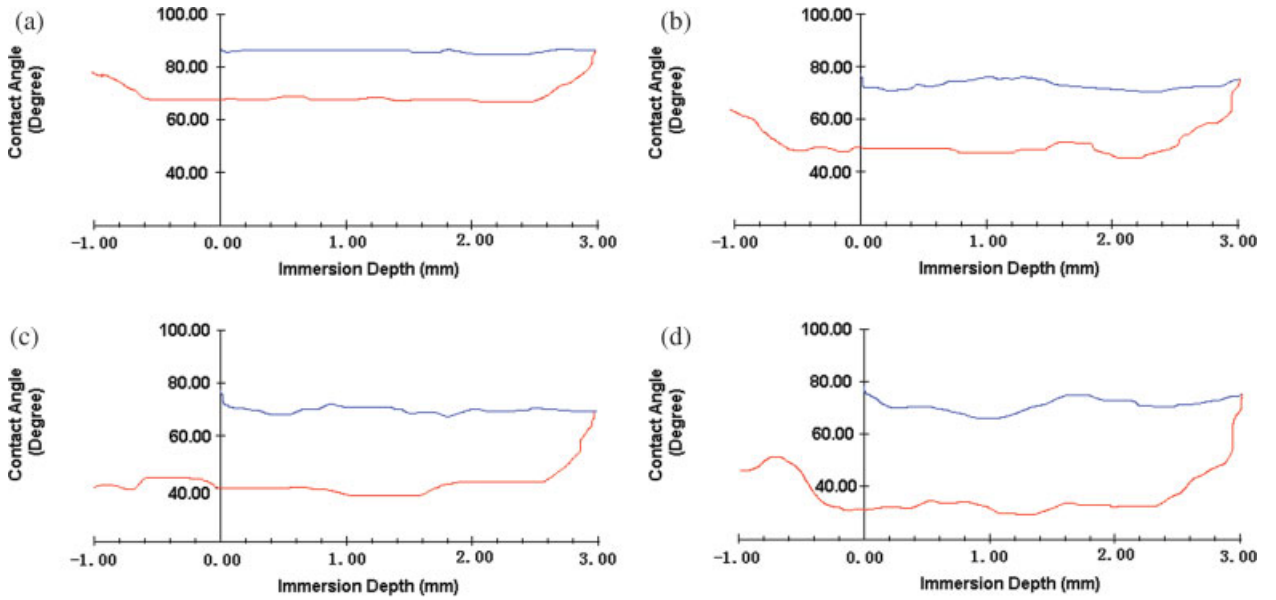

Figure 3 Dynamic contact angles of (a) the original PET fiber and the fiber with (b) 20-, (c) 50-, or (d) 100-nm coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

This study examined the functionalization of PET fibers sputter-coated by Cu with AFM, EDX, and dynamic contact angle measurements. The surface properties of the PET fibers were significantly affected by the functional coatings. The metallic coating of Cu obviously improved the conductivity of the fibers. The surface wetting behavior of the fibers was also altered by the sputter coating of Cu.

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