Surface Nanaostructure Evolution of Functionalized Polypropylene Fibers

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ABSTRACT: It is well-known that fiber surface characteristics affect friction, wetting, conductivity, and other performance properties. This paper reports the evolution of the surface nanostructures of meltblown polypropylene (PP) fibers during the process of plasma treatment followed by copper (Cu) sputter coating. The effects of plasma treatment and Cu sputter coating on the surface morphology, chemistry, and properties of the fibers were characterized using scanning probe microscope (SPM), environmental scanning electron microscopy (ESEM), and electrical analysis. The atomic force mode (AFM) and lateral force mode (LFM) in the SPM were used to scan the fiber surface. AFM observations revealed the evolution of the surface morphology formed by surface treatment. The LFM images also indicated the change in surface nanomechanical behavior. A full energy dispersive X-ray analysis (EDX) mounted on the ESEM was used to examine the change in the chemical compositions of the functional surfaces. The electrical properties of the functionalized materials were analyzed using electrical resistance test. The Cu sputter coating significantly altered the surface conductivity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1243–1247, 2007

Key words: surfaces; polypropylene; coatings; atomic force microscopy; fibers

INTRODUCTION

Fibrous materials have been produced in various forms such as yarns, threads, cords, ropes, cables, and fabrics. The porous structures of fibrous materials possess flexibility, air permeability, and integrity. They have been increasingly used in many industries for a variety of applications ranging from wipes, bandages filters, sorbents, and protective clothes.[1]

Fibrous materials processed by meltblowing provide the combination of fine fibers, random entanglement, and small pore size. Meltblown fabrics are manufactured directly from polymer resins. The resins in chip form are heated and extruded. The extruded fibers are attenuated by sonic-velocity air at 250–500°C. The fibers are then condensed (separated from the air stream) as a randomly entangled web consisting of discontinuous subdenier fibers.[2] Meltblown nonwovens have been widely used in filtration, separation, battery, and hygiene products.[3]

In these applications, the functions of meltblown materials are associated with such phenomena as wetting, biocompatibility, adsorption, and electrical conductivity. Wetting, biocompatibility, adsorption, and many other performance properties all begin at the surface. The properties of fiber surfaces and interfaces play key roles in material processing and application technologies.[4]

In recent years, surface modification of textile materials by plasma-related techniques has opened up new possibilities in this field. Plasma has long been recognized as a source of positive ions, photons, and chemically reactive atoms and molecular radicals.[5] It has been increasingly used in the etching, deposition, or other modifications of solid surfaces including various forms of textile materials to improve surface properties.[6] The most promising technique for the surface functionalization of textile materials in plasma-related techniques is sputtering,[7] which has been widely used to modify various materials in many industries.

The ability to deposit well-controlled coatings on polymer fibers would expand the applications of meltblown materials, based on changes to both the physical and chemical properties of polymer fibers. In this study, meltblown nonwoven substrate was functionalized using metal sputter coating. The effects of surface treatment on the surface morphology, chemistry, and properties of the fibers were characterized using scanning probe microscopy (SPM), environmental scanning electron microscopy (ESEM), and electrical analysis.

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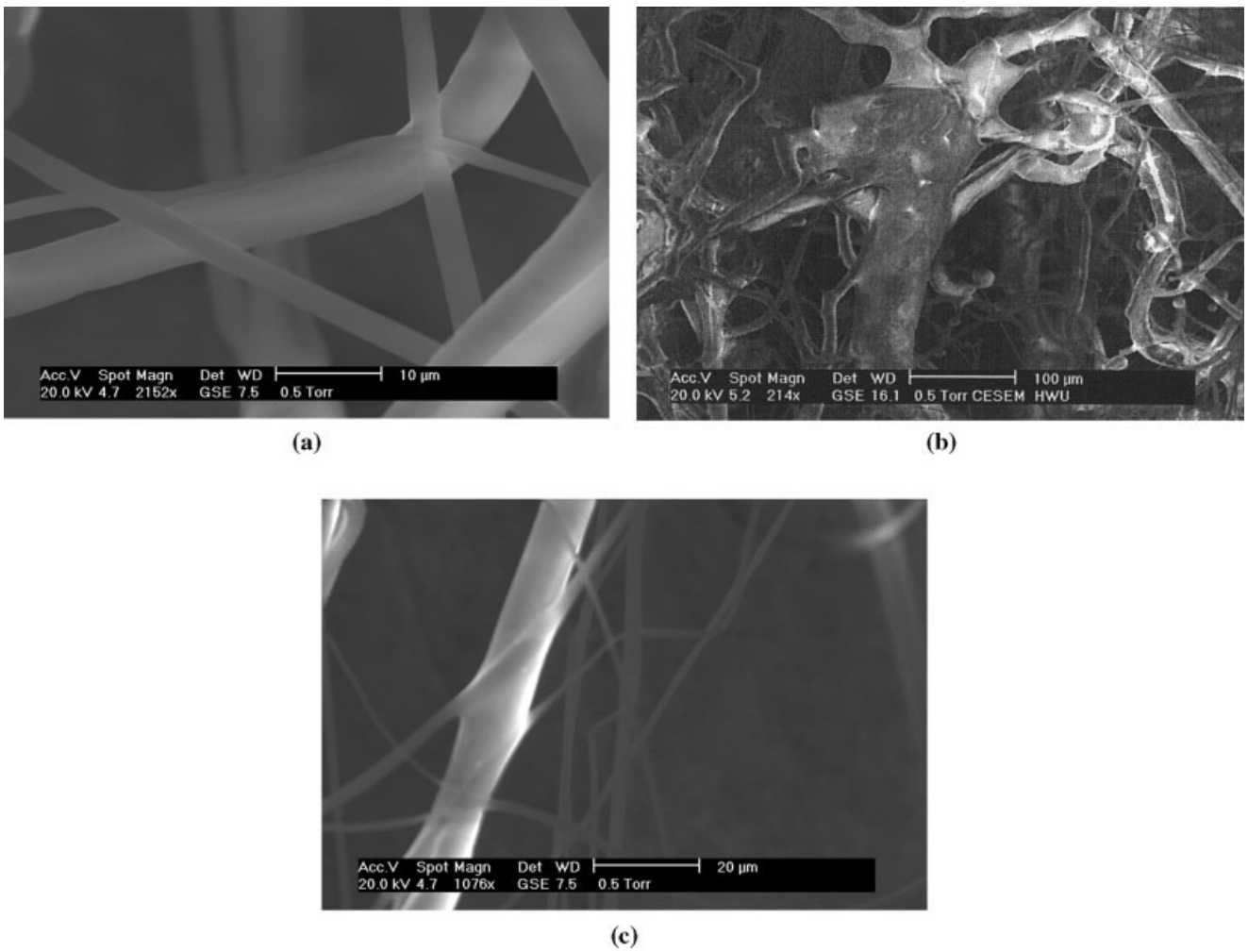

Figure 1 ESEM images of the material (a) original, (b) plasma treated, and (c) Cu coated for 10 min.

EXPERIMENTAL

Materials preparation

The substrate used in this study was polypropylene (PP) meltblown nonwoven with a base mass of 75 g/m^2. The material was washed with ethanol and distilled water before any treatments. After washing, the material was dried in an oven at about 40°C.

Before the sputter coating, the substrate was modified by oxygen plasma treatment to activate the surface. Plasma surface activation was made in a Europlasma CD 400M/PC laboratory system. The material was subjected to oxygen plasma treatment at 100 W power with a gas flow of 1.67 cm^3/s for 30 s.

After the surface activation, the substrate was functionalized by sputter coating. A magnetron sputter coating system was used to deposit a nanolayer on the substrate. A high-purity Cu target (99.999%) was mounted on the cathode, and the fiber substrate was placed on the anode with a side facing the target. Argon (99.99%) was used as the bombardment gas. The sputtering pressure was set at 3 Pa. The DC (direct current) power used for Cu sputtering was set at 100 W. The sputtering was performed on one side of the substrate for 10 and 20 min, respectively, at room temperature.

Nanostructural characterization

SPM

Scanning probe microscope (SPM), particularly in the form of atomic force microscopy (AFM), has been increasingly applied in textiles research.[8] The SPM used in this work was a Benyuan CSPM 4000. Scanning was carried out in contact mode AFM and lateral force mode (LFM) with a silicon cantilever. All images were obtained at ambient conditions. The scanning frequency was set at 2.0 Hz and the normal force applied on the cantilever was 2 nN.

ESEM

Environmental scanning electron microscope (ESEM) offers full functionality in the three modes of opera-

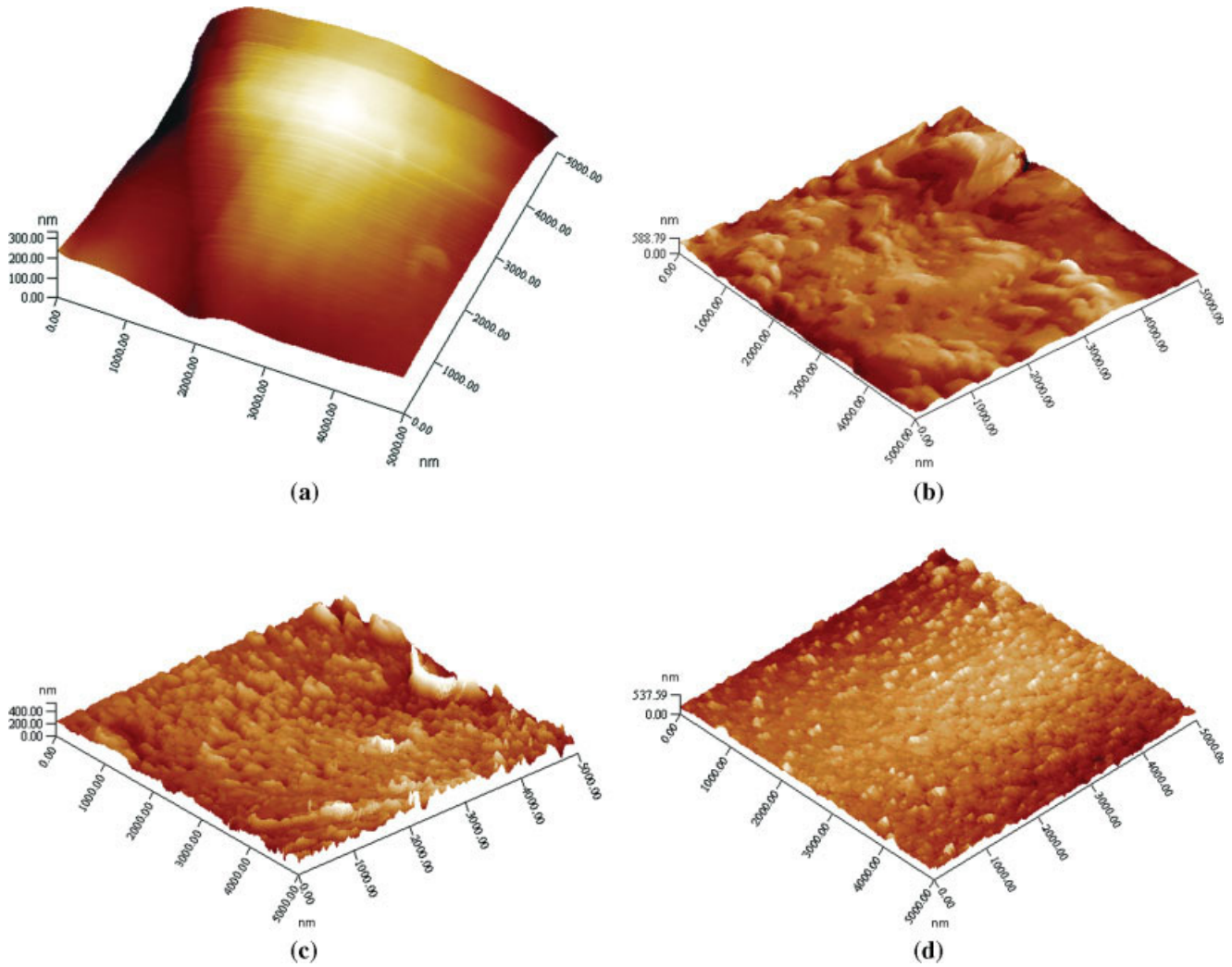

Figure 2 Evolution of surface morphology observed by AFM: (a) original, (b) plasma treated, (c) Cu coated for 10 min, and (d) Cu coated for 20 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion: high vacuum, low vacuum, and ESEM mode. A low vacuum mode is suitable for the examination of uncoated nonconductive samples, wet samples, and dynamic process.[9] The ESEM for this study was The Philips XL30 ESEM.

The Philips XL30 ESEM integrated with a Phoenix energy-dispersive X-ray detector adds extraordinary capabilities to the entire system. It allows analyzing of elemental compositions down to boron, including the light elements such as carbon, nitrogen, and oxygen. In this study, the fiber surface was examined by the EDX at an accelerating voltage of 20 kV with accounting time of 100 s.

Electrical properties

The electrical resistivity was measured using a collinear four-probe array based on the Chinese standard GB/T 14,141-1993. The apparatus used was SX1934 made by Baishen Technologies. The tests were performed three times for each sample, and the mean values were recorded and reported.

RESULTS AND DISCUSSION

Web structure of the substrate

The ESEM image in Figure 1(a) shows the web structures of the meltblown polypropylene nonwoven substrate. The fibrous structure of the substrate is clearly revealed in the image, but the image also reveals the variation of the fiber diameters in the web. The diameters of the fibers in the polypropylene meltblown web are in the range between 1 and 10 μm. The fibers in the web are randomly oriented and the pores with various sizes are formed by entanglement of fibers. The fiber surface looks quite smooth, although the surface details are not very clear at this magnification. The ESEM image Figure 1(b) display the nonwoven treated by gas plasma. Some particle-like structures are visible on the fiber surface, but more details need

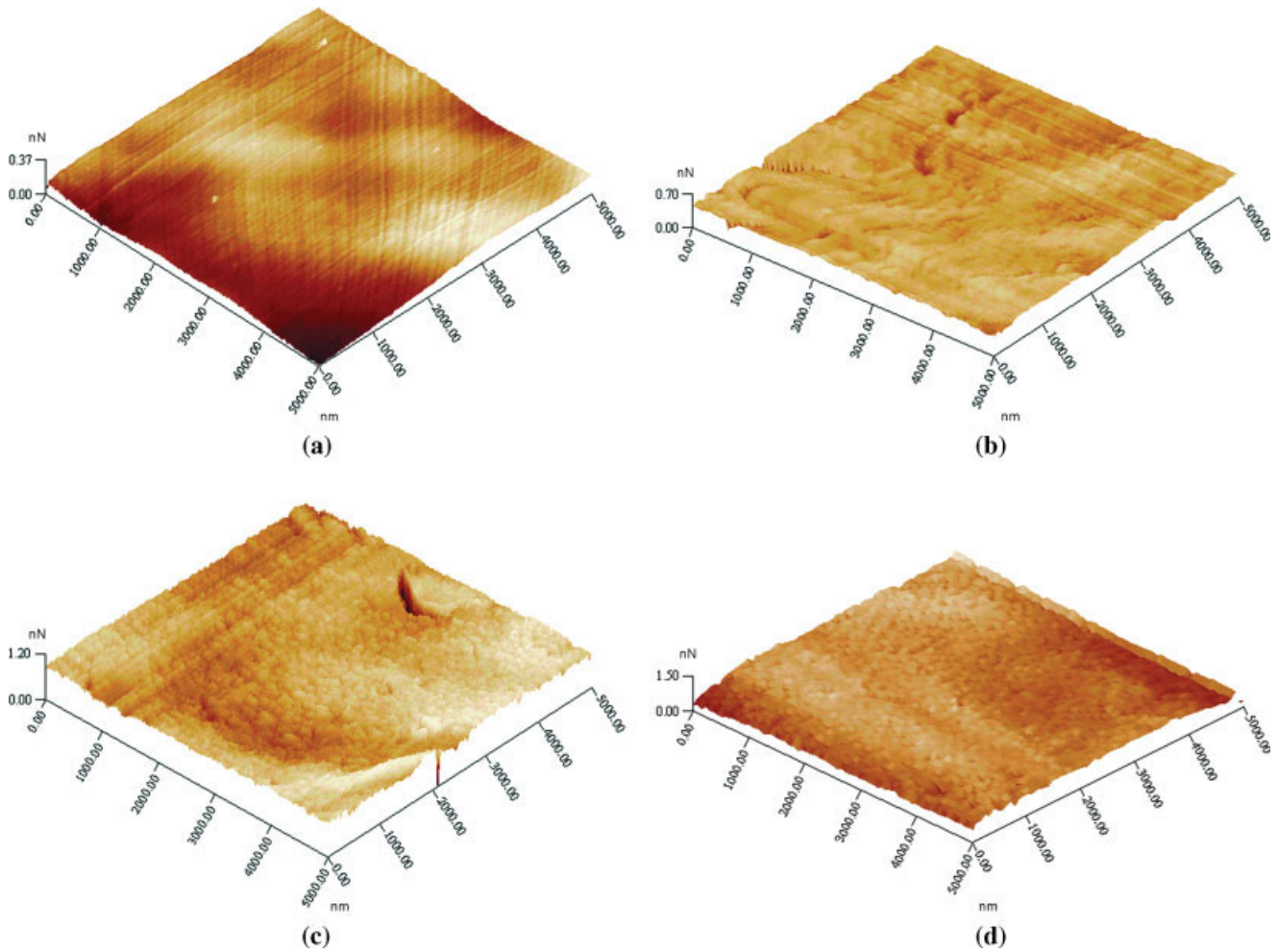

Figure 3 Evolution of surface nanomechanical property examined by LFM: (a) original, (b) plasma treated, (c) Cu coated for 10 min, and (d) Cu coated for 20 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to be analyzed. After the sputter coating of Cu, the fibers seem to become smooth again as illustrated in Figure 1(c). The coating structures are not very clear at this magnification. Therefore, the fiber surfaces were further analyzed with the scanning probe microscope.

Nanostructural evolution

The surface morphology of the fibers in the meltblown is presented in Figure 2. The AFM image in Figure 2(a) shows the relatively smooth surface of the fiber. The microfiber in the meltblown substrate does not show any fibril structures on its surface. The fibers in the meltblown substrate are formed by high velocity attenuation with hot air. Therefore, the fibers are not properly crystallized during the process.[10] Plasma activation significantly changes the surface characteristics of the fibers. AFM examination clearly reveals the effect of the plasma treatment on the surface morphology of the fiber. It can be seen from Figure 2(a) that the fiber surface is obviously roughened after plasma treatment. The plasma activation forms aggregate structures on the fiber

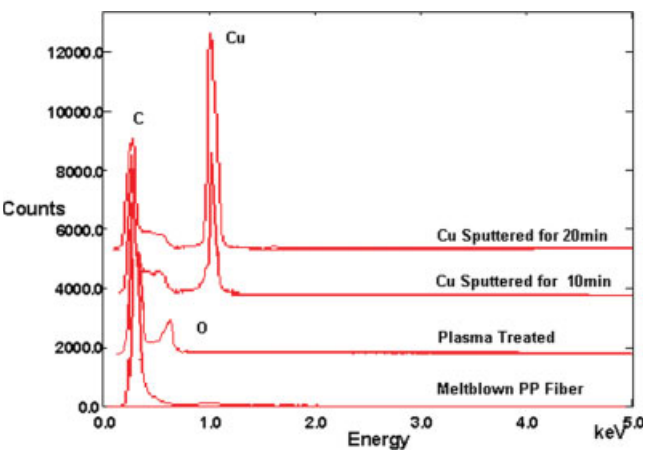

Figure 4 EDX spectra of fiber surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Resistance Measurement

Treatment	Resistivity (Ω cm)
Without treatment	Out of range (over 10^4)
Plasma treated	Out of range (over 10^4)
Cu sputtered for 10 min	0.95
Cu sputtered for 20 min	0.27

surface. The aggregates are created by etching effect of the plasma bombardment.

Figure 2(c,d) shows the surfaces of the polypropylene fiber sputter coated with copper for 10 and 20 min, respectively. It can be seen that, in the initial stage of the deposition, the nanoclusters of copper are clearly recognized on the fiber surface, as exhibited in Figure 2(c). The Cu clusters formed on the fiber surface have various sizes ranging from 10 to over 20 nm. The growth of the sputtered Cu nanocluster on the microfiber surface can be seen from Figure 2(d) as the deposition is increased to 20 min. It appears that the sizes of the sputtered Cu nanoclusters are increased as the sputter coating time is increased to 20 min and the Cu clusters become more compact, as illustrated in Figure 2(d). The size of the Cu clusters on the fiber surface is also increased to over 30 nm.

The nanomechanical properties of the fibers are also revealed by LFM observations. The details of the observations are shown in Figure 3. The surface of the original fiber shows very low surface friction, as illustrated in Figure 3(a). The LFM image indicates that the surface friction is less than 0.4 nN. The plasma treatment significantly increases the surface friction of the fiber, as shown in Figure 3(b). The increase of the surface friction is attributed to roughness of the surface caused by plasma etching. The FLM image in Figure 3(c) indicates the further increase of the surface friction of the fiber sputtered for 10 min. The nanoclusters formed on the fiber surface contribute to the increase in the surface friction. The surface friction is increased to about 1.5 nN as the sputter coating is expanded to 20 min, as presented in Figure 3(d). This behavior can be attributed to the nucleation and island formation on the fiber surface as Cu grains are growing.

EDX analysis

The funtionalization of the fiber surfaces is also confirmed by EDX analyses. The change in surface chemistry also reveals the nanostructural evolution, as presented in Figure 4. The EDX spectra of the fibers clearly indicate the chemical composition of the fiber. The PP fibers in the meltblown substrate dominantly consist of C. A small amount of O is detected on the fiber surface after plasma treatment, which indicates the introduction of some functional groups on the fiber surface. A significant amount of Cu on the fiber surface after sputter coating can be seen from the EDX spectra. The amount of Cu is significantly increased as the sputtering time is increased to 20 min. The EDX analysis reveals the chemical change during the nanostructural evolution.

Resistance measurement

The results of resistivity measurements of the substrate are listed in Table I. The meltblown substrate shows very high surface resistivity before any treatment. It seems that plasma treatment does not change the surface resistivity, as indicated in Table I. A significant decrease in surface resistivity is achieved after sputter coating. The surface resistivity of the substrate before sputter coating is over 10^3 Ω cm, indicating poor electrical conductivity. After the coating for 10 min, the surface resistivity of the substrate drops from over 10^3 to about 0.95 Ω cm. The increase in sputtering time can further lower the surface resistivity of the substrate, as presented in Table I. This is attributed to the thicker coating of the conductive copper layer on the fiber surface.

CONCLUSIONS

The effects of plasma treatment and Cu sputter coating on the surface morphology, chemistry, and properties of the fibers have been analyzed using SPM, ESEM, and electrical measurement. The evolution of the surface nanostructures and chemistry has resulted in the change in surface nanomechanical properties and conductivity. The surface of polymer fibers can be modified to improve surface properties based on the change in surface chemistry and physics for a variety of applications. The ability to deposit well-controlled coatings on polymer fibers would expand the applications of meltblown materials.

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