Surface Characterization and Properties of Functionalized Nonwoven

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ABSTRACT: Nonwoven materials have been increasingly used in many industries. The surface properties of nonwoven materials are of importance in these applications. In this study, functional nonwoven materials were prepared by sputtering deposition of copper (Cu), zinc oxide (ZnO), and polytetrafluoroethylene (PTFE) on the surface of polypropylene (PP) fibers. Atomic Force Microscopy (AFM) and Environmental Scanning Electron Microscopy (ESEM) were employed to study the surface morphology and chemical compositions. The observations by AFM revealed the formation of functional nanostructures on the fibre surfaces and the ESEM examination confirmed the formation of functional compositions on the fiber surface. The metallic coating of Cu significantly improved the surface conductivity of the material. The transmittance analysis indicated that the ZnO coating obviously increased the ultra-violet absorption of the material. The surface hydrophobicity of the nonwoven material was enhanced by the sputter coating of PTFE. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 132–137, 2008

Key words: fibers; AFM; coatings; functionalization of polymers; surfaces

INTRODUCTION

Fibrous materials have been increasingly used in various industries. In these applications, the fibrous materials in the form of nonwovens have shown the fastest growth in recent decades. Versatile nonwovens for a wide range of applications ranging from daily articles to high performance materials have been manufactured utilizing needlepunch, chemical, and thermal bonding, and other technologies.[1]

Nonwoven materials with special surface structures and properties are often required to meet the different needs of technical applications. The surfaces of nonwoven materials are of importance in various technical applications as the surface structures and properties affect abrasion, adhesion, electro-optical property, adsorption, and biocompatibility of the materials. However, the surfaces of polymer fibers in nonwoven materials are not often ideal for such particular applications such as electrical conductivity, light absorption, and wettability. Various techniques, such as physical vapor deposition (PVD), electroless deposition and sol-gel deposition, have been employed to modify the surface properties of textile materials.[2–4] The physical approach using sputter coating[5] has proven to be one of the most promising techniques for the functionalization of textile materials since the chemical techniques always cause some sort of pollution.

Magnetron sputter coating is one of the major technologies in PVD processes. Magnetron sputter coating is a vacuum process, which has been increasingly used to deposit thin functional coatings on various substrates for improving the surface properties of the materials. It is preformed by applying a high voltage across a low-pressure gas to create plasma, which consists of electrons and gas ions in a high-energy state. During sputter coating, energized gas ions strike a target, composed of the desired coating material, and cause atoms from the target to be knocked off with high energy to travel to and bond with the substrate, forming a functional coating on the surface of the substrate. Magnetron sputter coating offers such advantages as uniform and compact, stronger bonding between coating and its substrate and environmentally friendly.[6]

The ability to deposit well-defined layers on nonwoven materials would expand the applications of the materials, based on changes to both the physical and chemical properties of nonwoven materials. In this study, polypropylene (PP) meltblown nonwoven was functionalized with the coatings of copper (Cu),

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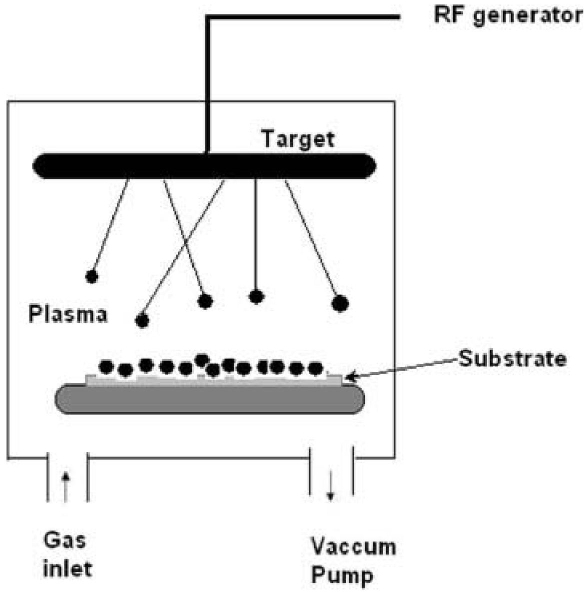

Figure 1 Sputter coating.

zinc oxide (ZnO), and polytetrafluoroethylene (PTFE) by sputtering technique. Atomic Force Microscopy (AFM) was employed to study the surface structures. The surface chemical structures were examined by energy dispersive X-ray analysis system (EDX) in the environmental scanning electron microscopy (ESEM). The surface properties of the functionalized nonwoven materials were characterized by electrical resistance test, optical test, and contact angle measurement, respectively.

EXPERIMENTAL

Materials preparation

The nonwoven material used in this study was PP meltblown nonwoven with a mass per area unit of 60 g/m^2. The samples of the nonwoven material were washed by acetone in an ultrasonic bath for 5 min and then dried at room temperature.

A magnetron sputter coating system supplied by Shenyang Juzhi, Ltd. was used to deposit the nanostructured Cu, ZnO, and PTFE onto the surface of PP nonwoven substrate at room temperature, respectively. High purity Cu, ZnO and PTFE targets were used and the sputtered particles were deposited on the side of the nonwoven substrate facing the target, as illustrated in Figure 1. The coatings were performed using radio frequency (RF) sputter coating. To avoid the deformation of substrate caused by high temperature, water-cooling was used to control the temperature of the substrate during the sputtering process. The sputtering chamber was first evacuated to a base pressure of 5×10^{-4} Pa prior to introducing the high purity argon gas as bombardment gas. During the sputtering, the substrate holder was rotating at a speed of 100 rpm to ensure the sputtered particles uniformly deposited on the substrate. The sputtering conditions are listed in Table I.

TABLE I
Sputtering Conditions

Target	Pressure (Pa)	Power (w)	Time (min)
Cu	0.5	150	60
			120
ZnO	0.5	150	60
			120
PTFE	0.5	150	60
			120

Surface characterization

Surface morphology

The scanning probe microscope used in this work was a CSPM4000 AFM made by Benyuan Company LTD. Scanning was carried out in contact mode AFM[7] and all samples were scanned at room temperature in atmosphere. The scanning size was 5000 $\times$ 5000 nm^2, and the scanning frequency was set at 1.0 Hz. The tip used was CSC11 with a nominal spring constant of 0.35 N/m.

Energy dispersive X-ray analysis

The ESEM Philips XL30 integrated with a Phoenix energy-dispersive X-ray (EDX) detector added extraordinary capabilities to the entire ESEM system. It allowed analyzing of elemental compositions down to boron including the light elements such as carbon, nitrogen, and oxygen. The charging artefacts could be eliminated because of the existence of gas in the ESEM chamber.[8] In this study, the nonwoven surface

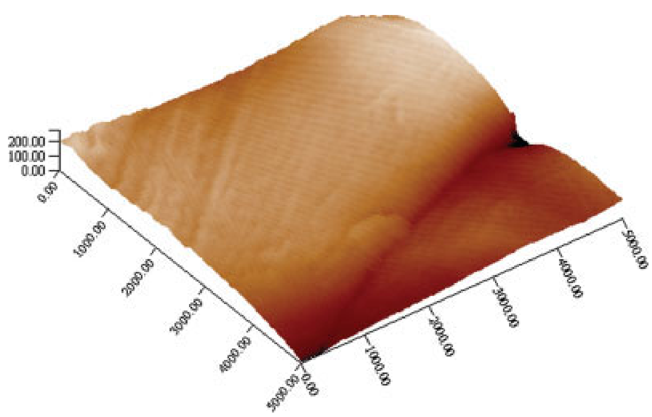

Figure 2 AFM images of the PP fiber of the metblown nonwoven. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

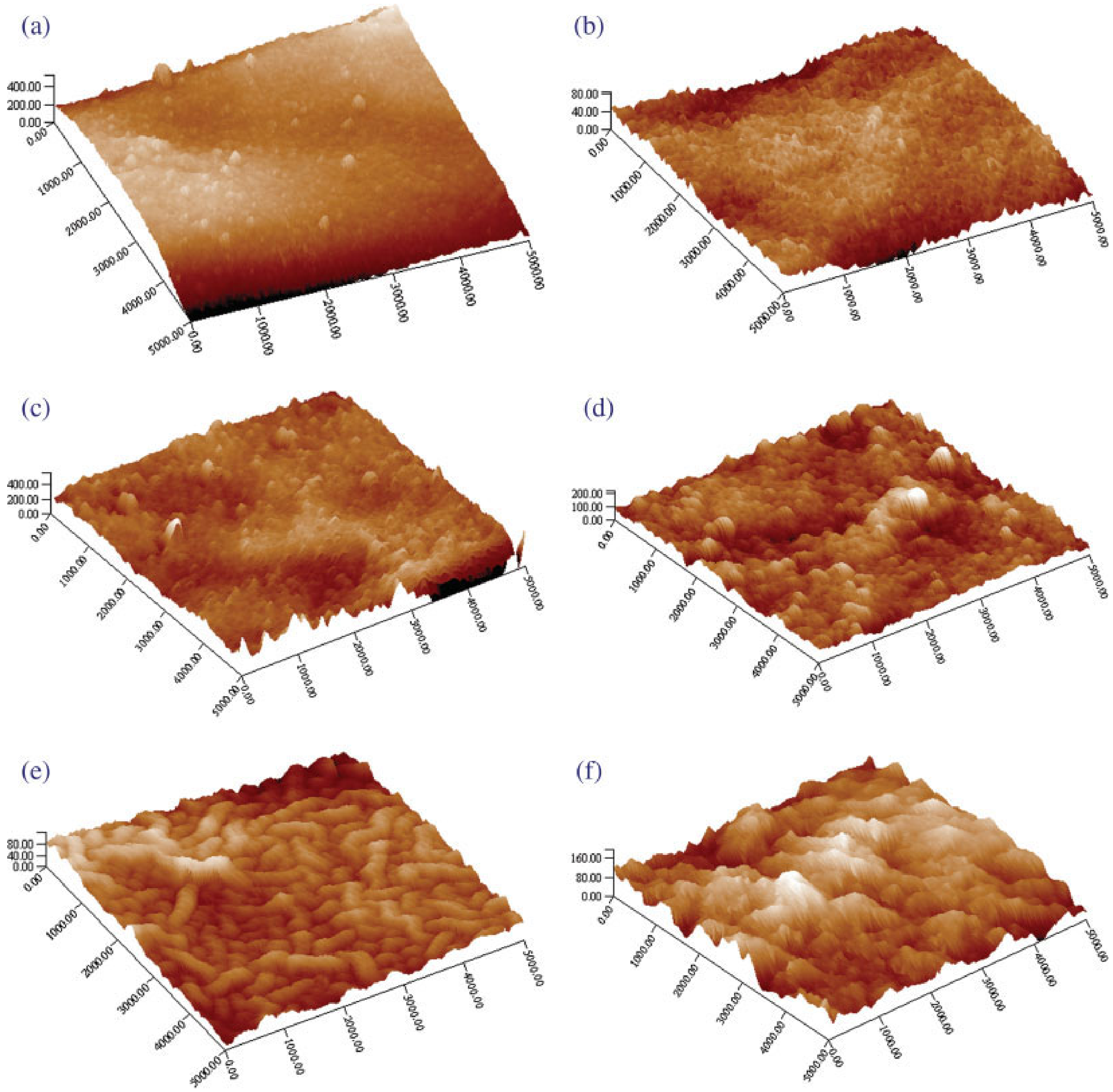

Figure 3 AFM images of the sputter coated PP fiber: (a) Cu for 60 min; (b) Cu for 120 min; (c) ZnO for 60 min; (d) ZnO for 120 min; (e) PTFE for 60 min; (f) PTFE for 120 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was examined by the EDX analysis at an accelerating voltage of 20 kV with accounting time of 100 s.

Surface properties

Surface resistivity

The electrical resistivity was measured using a collinear four-probe array. The apparatus used was SX1934 made by Baishen Technologies. To minimize the deviations brought by the unevenness of textile surface, the resistivity of each sample was measured three times, and the average values were used.

Optical property

The optical properties of the material were examined by ultra-violet and visible light (UV/Vis) absorbance analysis. The UV/Vis absorbance spectrum was obtained by passing different wavelengths of light ranging from 200 to 600 nm through a nonwoven sample. The UV/Vis spectroscopy used was a Perkin-Elmer Lambda 900.

TABLE II
Surface Roughness

Materials	PP	Cu coated 60 min	Cu coated 120 min	ZnO coated 60 min	ZnO coated 120 min	PTFE coated 60 min	PTFE coated 120 min
Roughness (nm)	4.05	8.09	10.02	9.28	12.23	15.67	17.45

Contact angle

The surface wetting behavior of the functionalized materials was examined by contact angle measurement. Contact angle measurement was performed using DSA100 Drop Shape Analysis System produced by KRUSS. De-ionized water was dropped onto the sample from a needle on a microsyringe during testing. A picture of the drop was taken a few seconds after the drop set onto the sample. Static contact angles could then be calculated by the software through analyzing the shape of the water drop.[9]

RESULTS AND DISCUSSION

Surface morphology

The AFM image reveals the fiber surface of the uncoated nonwoven material, as presented in Figure 2. It clearly shows that the uncoated PP fiber has a relatively smooth surface with some groove-like structures on it. These structures are probably formed during the process of meltblowing, leading to the formation of the tiny grooves along the fiber axis.

The sputter coatings of Cu, ZnO, and PTFE significantly alter the surface characteristics of the PP fibers

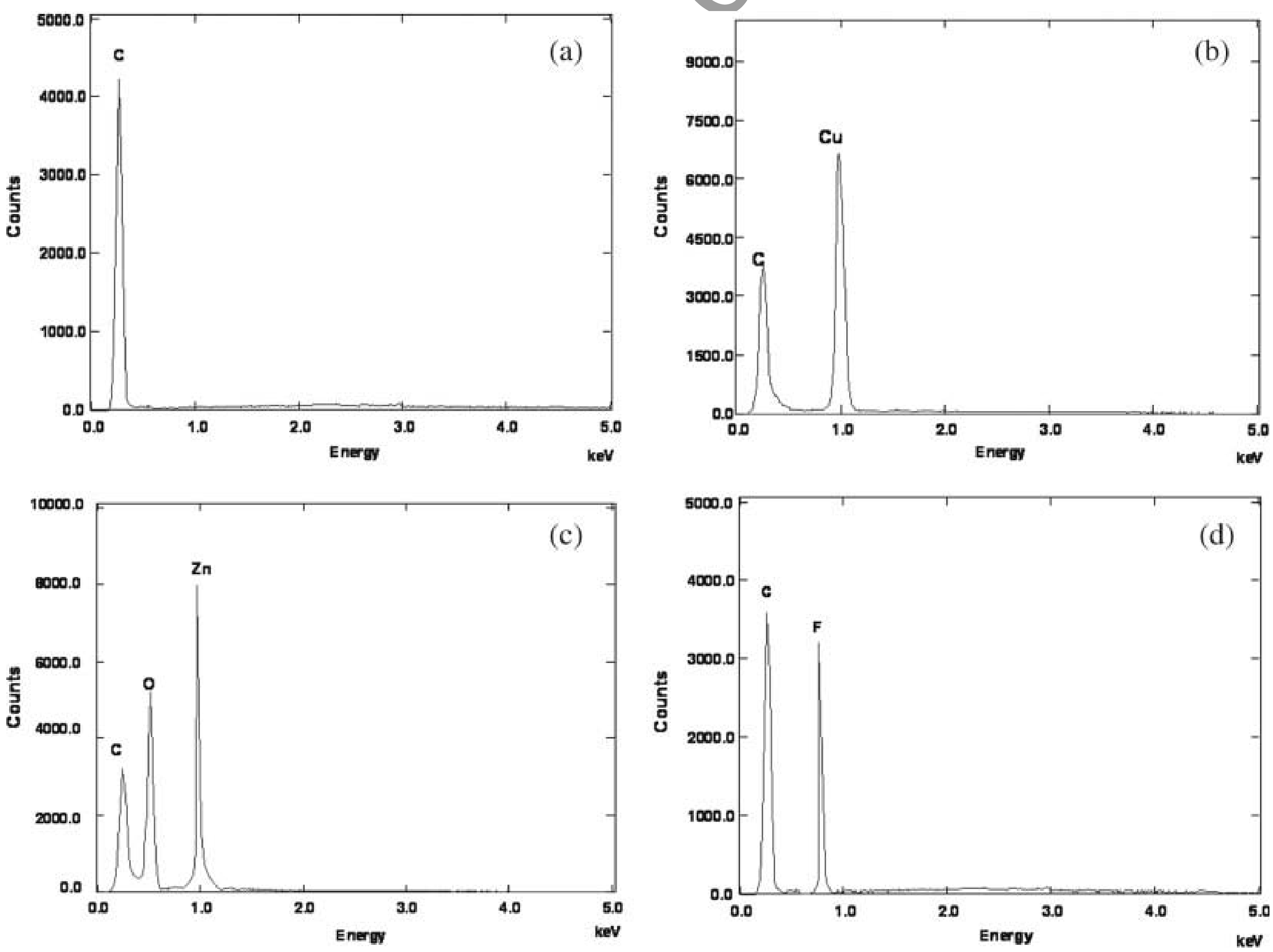

Figure 4 EDX spectra of the sputter coated PP fiber: (a) uncoated; (b) Cu coated; (c) ZnO coated; (d) PTFE coated.

TABLE III
Surface Resistivity

Materials	PP nonwoven	Cu coated		ZnO coated		PTFE coated	
		60 min	120 min	60 min	120 min	60 min	120 min
Resistivity (Ωcm)	Over 10^6	54.3	0.36	Over 10^6	Over 10^6	Over 10^6	Over 10^6

in the nonwoven material, as revealed in Figure 3. The Cu clusters scatter on the PP fiber surface after coating for 60 min. The Cu clusters have variable sizes from less than 20 nm to over 30 nm, as illustrated in Figure 3(a).The average size of the sputtered Cu cluster is about 24.6 nm. As the coating time is increased to 120 min, the Cu clusters coated on the PP fiber surface look more even and the average size of the sputtered Cu clusters is increased to about 34.5 nm, as revealed in Figure 3(b). This is attributed to the collision of the sputtered Cu grains. The increase in sputter coating time leads to the growth of the Cu clusters and more compact deposition. The observations reveal that the formation and the growth of of the deposited Cu nanoparticles on the fiber surface.

The sputter coating of ZnO forms aggregation structures on the PP fibers of the nonwoven, as displayed in Figure 3(c,d). The ZnO aggregations grow from 36.8 nm for 60 min coating, to 52.3 nm for 120 min coating. The increase in sputter coating time also leads to the growth of the ZnO aggregations and more compact deposition on the PP fiber surface. The PTFE coating; however, forms ribbon-like structures on the PP fibers of the nonwoven, as exhibited in Figure 3(e,f). They are quite different from the nanoparticle structure of Cu coating and the nano-aggregation structure of ZnO coating. The increase in sputter coating time also leads to the growth of the PTFE ribbon structures, as shown in Figure 3(f). The different structures of the sputtered ZnO and PTFE formed on the fiber surface are attributed to the chemical nature of the ZnO and PTFE and the internal bonding of the molecules.

The functional nanostructures formed on the fiber surface change the surface roughness as revealed in Table II. It can be seen that the surface roughness is increased as the coating thickness is increased. This is attributed to the collision and growth of the sputtered nanoculsters. The surface roughness is also affected by the form of the functional nanosctrutres deposited on the fiber surface. The ribbon-like structures of PTFE shows the highest roughness and the particle-like Cu shows the lowest roughness, which confirms the AFM observations.

EDX analysis

The funtionalization of the PP nonwoven surfaces by sputter coatings of Cu, ZnO, and PTFE is also confirmed by EDX analyses. The EDX spectra in Figure 4 show the PP nonwoven material before and after the sputter coatings of Cu, ZnO, and PTFE, respectively. It can be seen from Figure 3(a) that the surface of the nonwoven material dominantly consists of C before the sputter coating. The composition of hydrogen (H) in the material is too light to be detected in the EDX analysis. A significant amount of Cu on the nonwoven surface after Cu sputter coating for 60 min can be seen in the spectrum, but the amount of C is reduced in the EDX spectrum, indicating the coverage of the surface by Cu coating as displayed in Figure 4(b). The EDX spectrum in Figure 4(c) shows the significant increase of the components of Zn and O as the ZnO coating is performed for 60 min. The PTFE coating is also confirmed by the EDX spectrum in Figure 4(d), indicating the component of C and F on the surface of the material.

Surface resistivity

The results of the electrical resistivity tests for the nonwoven samples are given in Table III. The uncoated PP nonwoven has a very high surface resistance, but the metallic sputter coatings of Cu reduce the surface resistance significantly. The test results clearly show that the surface resistivity drops

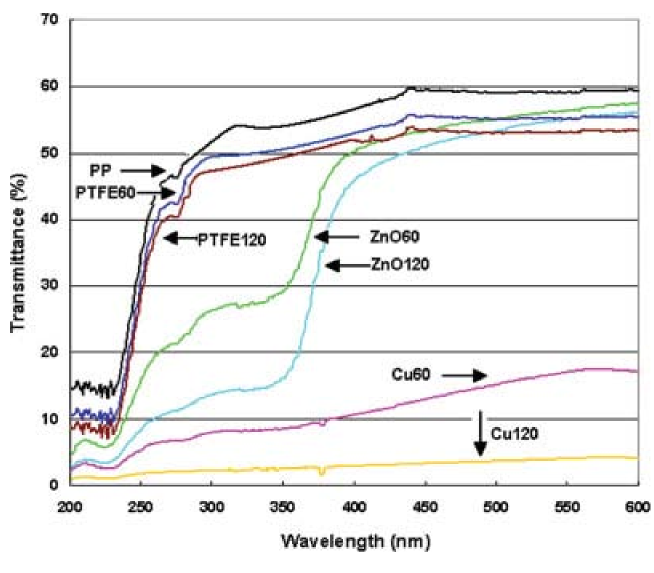

Figure 5 UV/Vis spectra of the material with different coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Contact Angles

Materials	PP nonwoven	Cu coated		ZnO coated		PTFE coated	
		60 min	120 min	60 min	120 min	60 min	120 min
Contact angle (°)	95	85	84	78	79	125	128

to about 54.3 Ωcm, as the Cu coating is performed for 60 min. The surface resistivity of the nonwoven material is further reduced to about 0.36 Ωcm, as the Cu coating is extended to 120 min, indicating better surface conductivity. The ZnO and PTFE coatings; however, show the surface resistivity over 10^6. This is attributed to the nature of the sputtered material.

Optical properties

The optical properties of the nonwoven coated with difference materials are presented in Figure 5. It shows the transmittance of the UV and visible light through the nonwoven. The uncoated nonwoven shows the transmittance of over 50% in the wavelength range from 300 to 600 nm, indicating the good transmittance of visible light of the uncoated PP nonwoven. The transmittance drops gradually to about 15% in the range between 300 and 200 nm, showing the UV shielding effect of the material. The sputter coatings by metallic component of Cu considerably reduce the transmittance of the materials both in the UV and visible light ranges as illustrated in Figure 5, indicating the light absorption effect of the Cu coating. The transmittance is further reduced as the coating time is increased to 120 min because of the thicker coating of the Cu clusters on the material.

Figure 5 also clearly indicates that the average transmittance of the ZnO coated samples over the wavelength range between 400 and 600 nm exceeds 50%, which is close to that of the uncoated nonwoven, revealing the transparent property of the ZnO coatings in visible light range. The absorption of ultra-violet (UV) from 250 to 350 nm by the ZnO coated samples is obviously observed in Figure 5. It is also found that the ZnO coating for 120 min shows better UV absorption than the 60 min coating. The UV absorption of the ZnO coating is attributed to its chemical structure of the material.[10] The PTFE coatings do not show any significant effect on the light transmittance of the materials, as revealed in Figure 5.

Surface wetting

The effect of the coatings on surface wettability is revealed by contact angle measurement, as indicated in Table IV. It can be seen that the untreated nonwoven has an average contact angles about 95°, indicating the hydrophobic behavior of the material. This hydrophobicity is enhanced by PTFE coating. The PTFE coating increases the contact angle to over 120°. This is attributed to the chemical nature of PTFE[11] and the increased surface roughness formed by the sputtered PTFE nanostructures. The Cu and ZnO coatings; however, lower the contact angles to less than 90°, as revealed in Table IV. The Cu and ZnO sputter coatings change the surface from hydrophobic to hydrophilic. The contact angle measures reveal that the sputter coatings may alter the surface wetting behavior of the nonwoven materials depending on the chemical properties of the deposited substance.

CONCLUSION

This study has examined the functionalization of PP nonwoven material by the sputter coatings of metallic, metal oxide, and polymeric substances. The surface properties of the material were significantly affected by the functional coatings. The metallic coating of Cu obviously improved the conductivity of the nonwoven material. The transparent ZnO coating showed the significant UV absorption of the material. The surface coated with PTFE exhibited the high contact angle, indicating enhanced surface hydrophobic behavior.

Sputter coating provides new approaches to the surface functionalization of textile materials for a wide range of applications, such as anti-static, UV absorption, and electromagnetic shielding materials.

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