Surface Functionalization of Polypropylene Nonwovens by Metallic Deposition

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ABSTRACT: In this study, melt-blown polypropylene (PP) nonwovens were used as substrates for the metallic deposition of copper. The substrates were pretreated by O_2 plasma, followed by treatments such as sensitization, activation, and reduction. The effects of the copper sulfate concentration, reaction temperature, and plasma power on the conductivity and adhesion strength of the PP nonwovens were investigated after copper deposition. The morphology of the PP nonwovens after copper deposition, analyzed by scanning electron microscopy and atomic force microscopy, revealed that copper nanoclusters were deposited on the fiber surface with a smooth surface morphology and dense structure. X-ray photoelectron spectroscopy indicated that the copper was present mainly in the form of the elementary substance, which coexisted with a little Cu^{2+}. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1624–1630, 2010

Key words: adhesion; coatings; cold plasma; fibers; surfaces

INTRODUCTION

With the increasing use of electronic communication products and instruments, electrostatic interaction and electromagnetic interference (EMI) have been considered a ubiquitous hidden danger in our daily life, especially as a potential threat to human health. Studies on electrostatic materials and EMI materials have attracted comprehensive attention recently. Textile materials with large specific surface areas, distinctive network structures, and excellent portability have great potential in diverse applications for electrostatic shielding.[1] However, common textile materials are not electrically conductive because of the chemical inertness of the polymer fibers used. Various techniques have been tried on the surface modification of polymer fibers to obtain good conductivity. The use of nanosized particles as fillers to prepare composite fibers[2] or just to attach to the fiber surface by their addition into the postfinishing agents of polymer fibers[3] are commonly used techniques. However, the agglomeration and negative effects on the fiber properties resulting from nanosized particles are always problems existing in the preparation processes. Physical methods, such as metallic vacuum evaporation[4] and sputter coating, provide new approaches to the surface functionalization of textiles. The coatings obtained by the aforementioned methods are easy to control and of good adhesive strength, especially when they are combined with plasma pretreatment.[5–7] However, physical modifications have their own limitations because of high costs or low efficiency. In addition, the requirement of a high temperature in the vacuum evaporation process could prevent the use of some metal materials or alloys with high melting temperatures.

Electroless deposition has become a widely used technique for the surface modification of polymers because of its advantages of uniform deposition and low cost, and no current, high vacuum, or high temperatures is required in this process.[8] In this study, the surface functionalization of polypropylene (PP) nonwovens by the electroless deposition of copper was attempted to obtain flexible–conductive materials for potential use in antistatic filtration, electromagnetic shielding, and intelligent textiles. Environmentally friendly plasma treatment was also applied to replace the traditional chemical solutions for the

pretreatment of the PP nonwovens in this study. The effects of the experimental parameters, including plasma power, copper sulfate ($CuSO_4$) concentration, and reaction temperature, on the conductivity and adhesion strength of the copper-deposited PP non-wovens were also investigated and discussed.

EXPERIMENTAL

Preparation of the materials

Spun-bonded PP nonwovens with a mass of 50 g/m^2 (Wantong Co., Ltd, Hangzhou, China) were used as the substrates for the metallic deposition of copper. The nonwoven samples were pretreated by O_2 plasma, and metallic deposition was carried out by multistep processes, including sensitization, activation, and reduction.

Plasma treatment

O_2 plasma pretreatment was performed in HD-1A low-temperature plasma machine (Zhongke Co., Ltd, Changzhou, China). The plasma treatment was set for 60 s with a power of 30 or 70 W and a vacuum-chamber pressure of 30 Pa.

Metallization process

Shortly after they were pretreated by O_2 plasma, the specimens were sensitized by immersion into an aqueous solution containing 12 g/L $SnCl_2$ and 40 mL/L HCl (36–38% w/w aqueous solution). Activation was performed by the immersion of the specimens into 50 mL of a 2 g/L $AgNO_3$ solution for 5 min. Simultaneously, 25% w/w ammonia water was added to the activation solution drop by drop until the initially turbid solution clarified. To prevent the activating agent Ag^+ on the fiber surface from entering the following metallic deposition, reduction was carried out in advance in a solution containing 1 mL of deionized water and 9 mL of formaldehyde.

The specimens were then immersed in the copper deposition bath for approximately 90 min. Table I gives the details of the chemicals used for copper deposition. The volume ratio of solution A to solution B was 3 : 1. The reaction temperature was held at 33–53°C. Ammonia water was used to adjust the pH value to above 11.

Surface morphology

The surface morphology of the nonwoven fibers was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM microscope used in this study was a Hitachi S4800 (Hitachi Ltd, Tokyo, Japan), and the AFM micro-

TABLE I
Chemicals Used for Copper Deposition

Solution A	Potassium sodium tartrate ($C_4H_4KNaO_3\cdot4H_2O$)	15 g/L
	Sodium hydroxide (NaOH)	10 g/L
	Sodium carbonate (Na_2CO_3)	4 g/L
	Potassium ferrocyanide ($K_4Fe[CN]_6\cdot3H_2O$)	0.1 g/L
	2,2′-Bipyridyl ($C_{10}H_8N_2$)	20 mg/L
	Disodium ethylenediamine ($Na_2H_2EDTA\cdot2H_2O$) Tetraacetate	15 g/L
Solution B	Copper sulfate ($CuSO_4$)	25 g/L
	Nickel chloride ($NiCl_2$)	4 g/L
	Formaldehyde (HCHO)	30 mL/L

scope was a CSPM4000 scanning probe microscope (Benyuan Co., Ltd., Guangzhou, China). AFM scanning was carried out in the contact mode, and all specimens were scanned under ambient conditions. The tip used was a CSC11 silicon probe (Mikro-Mash, San Jose, CA) with a curvature radius of less than 10 nm and a spring constant of 0.35 N/m. The scanning frequency was set at 1.0 Hz.

Component analysis

The composition and chemical state of copper on the nonwoven fibers after copper deposition was investigated with an Escalab MK II X-ray photoelectron spectroscopy (XPS) apparatus (VG Scientific, Sussex, United Kingdom). Equipped with an Al/Mg double-line anodic X-ray source, the sensitivity of the instrument was 1×10^5 cps, and the resolution was 0.9 eV with Mg Kα X-ray as an excitation source.

Surface resistance

The surface resistance of the copper-deposited PP nonwovens was measured as the sheet resistance (mΩ/sq, where sq represents an area of any size) by a four-point probe (SX1934, Baishen Technology, Suzhou, China). Four probes, with diameters of 0.5 mm, were all made by tungsten carbide, and the distance between each two probes was 1 mm. The samples were all tested 20 times in the same direction, and then, the average values were obtained.

Adhesion strength

Adhesion strength was characterized by a LRXPlus material mechanical testing machine (Lloyd Instruments, West Sussex, UK) at a 220 V + 10% working voltage. Before testing, specialized tape (3M600) was used to bond the specimens (1 in. wide, 7 cm long)
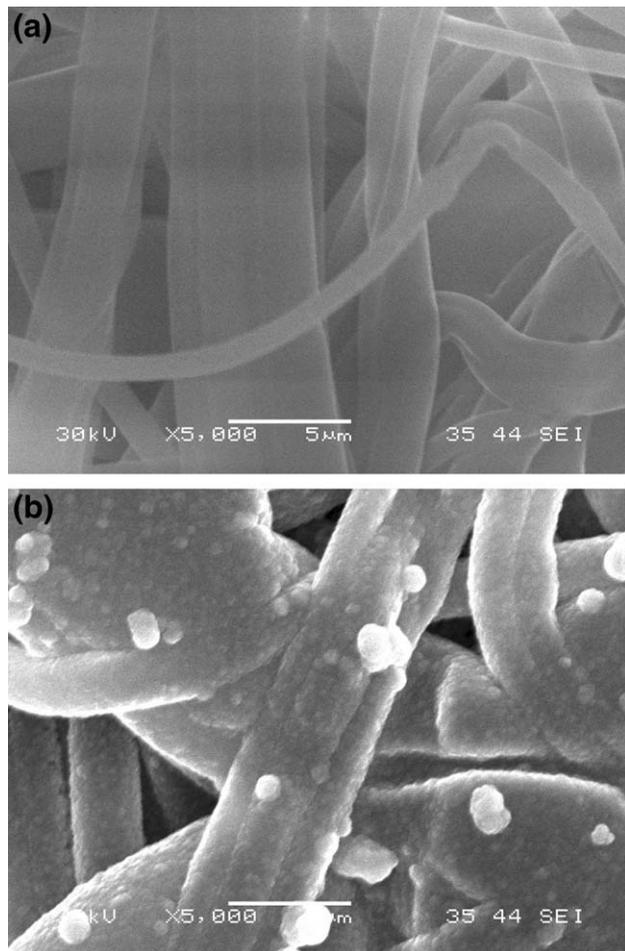
Figure 1 SEM images of the PP nonwovens: (a) uncoated and (b) copper-coated.

with a 400-g test load for 60 min. Then, the test load was taken away, and we left the specimens idle for 12 h to make sure that the specimen and tape were closely bonded. All experiments were conducted on a clean, flat workbench.

## RESULTS AND DISCUSSION

Surface morphology

Figure 1 shows the SEM images of the PP nonwoven fibers without and with copper deposition. The images clearly reveal the three-dimensional fibrous structures and surface morphology of the PP nonwoven fibers. As shown in Figure 1(a), the PP nonwoven fibers without copper deposition had a smooth surface. However, it was obvious that the fiber surface was uniformly and compactly covered with metallic particles, as shown in Figure 1(b). There also appeared to be some particle aggregates, which indicated Volmer–Weber growth of the copper films. The porous structure of the nonwoven made it possible to coat the entire fiber with the metal, except

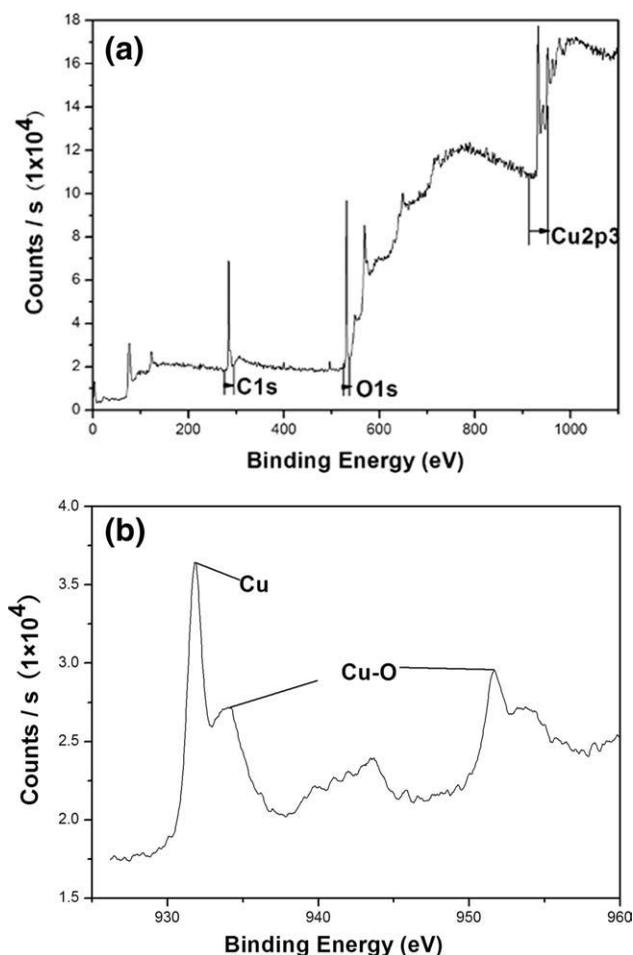perhaps for the unexposed regions of overlap where the fibers touched each other.

Further verification for the morphology of copper deposition was confirmed by AFM scans, as presented in Figure 2. As shown in Figure 2(a), the metal clusters deposited on the PP nonwoven fibers grew in an island pattern. With good distribution, the particles presented in a nanostructure with an average diameter of 164 nm in clusters and appeared to be uniform and dense, as revealed at a high magnification in Figure 2(b).

Surface chemistry

The results of the composition and chemical state of copper deposited on the PP nonwoven fibers characterized by XPS are represented in Figure 3. The characteristic peaks of the functional groups were revealed by the XPS spectra of C1s, O1s, and Cu2p3, as shown in Figure 3(a). Additional details for the XPS spectra of Cu2p3 are displayed in Figure 3(b).
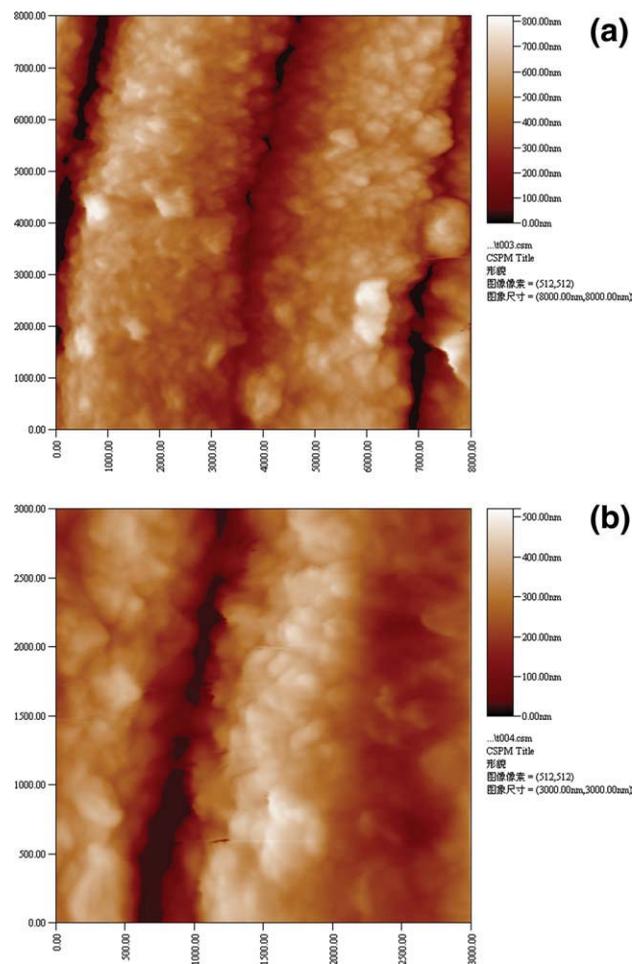
Figure 2 AFM images of the coated fibers: (a) 8000 nm × 8000 nm and (b) 3000 nm × 3000 nm. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 4 Effects of the $CuSO_4$ concentration on the surface resistance (vacuum degree = 30 Pa, reaction power = 50 W, pretreatment time = 1 min, reaction temperature = 38°C).
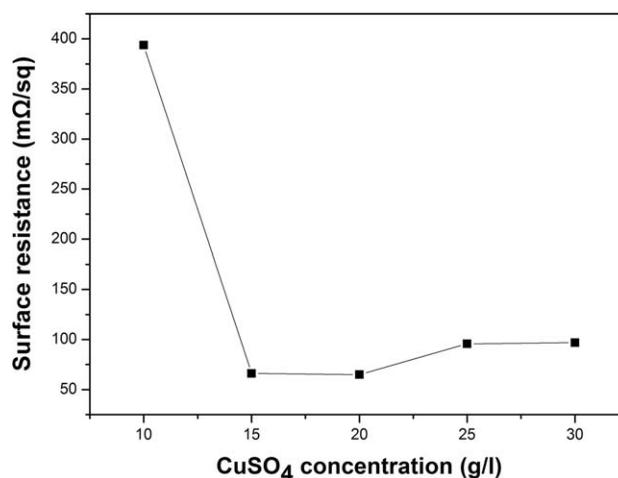
Figure 3 XPS spectra of the copper-deposited PP fibers: (a) C1s, O1s, and Cu2p3 and (b) Cu2p3.

Compared with data reported by Wu and other authors,[9–11] the binding energies of the characteristic peaks are listed in Table II.

As shown in Figure 3(a) and Table II, both C—C and C—H bonds existed on the PP nonwoven fibers. In addition, the peaks for the functional groups, such as O—H, O—C=O, and C=O, appeared in the spectra because of the oxygen plasma pretreat-

ment.[12] Figure 3(b) reveals a Cu2p3 peak at 931.78 eV corresponding to Cu. The significant peak of Cu indicated that the Cu deposition on the PP nonwoven fibers mainly existed in the form of simple copper. The peaks at both 933.9 and 942.17 eV corresponded to Cu—O. In addition, there was a peak at 530.06 eV, which also corresponded to Cu—O.
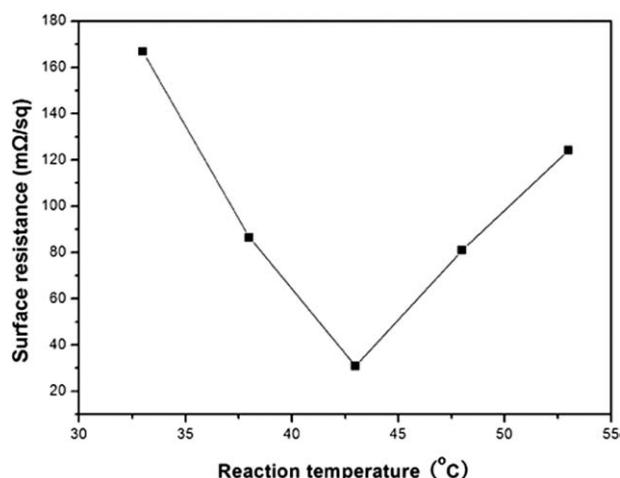
Surface resistance

Effect of the $CuSO_4$ concentration on the conductivity

Figure 4 shows the effect of $CuSO_4$ concentration on the surface conductivity of the PP nonwovens after copper deposition. The $CuSO_4$ concentrations used in the experiments were 10, 15, 20, 25, and 30 g/L.

As shown in Figure 4, the surface resistance appeared to be as high as 393.7 mΩ/sq when the $CuSO_4$ concentration was 10 g/L. It dropped rapidly from 393.7 mΩ/sq to 65 Ω/sq as the $CuSO_4$ concentration increased to 15 g/L. However, the surface resistance showed a slight increase with further increases in the $CuSO_4$ concentration from 15 up to 30 g/L. This increase tended to be relatively small, with the value maintained in the range between 65 and 100 mΩ/sq.

This phenomenon was attributed to the following facts: when the Cu^{2+} concentration in solution was very low, the deposition rate was slow. Thus, the metal film was relatively thin; this led to a high surface resistance of 393.7 mΩ/sq. However, when the Cu^{2+} concentration in solution became very high, the deposition rate was quite fast, and the metal film was uneven in thickness and rough on the surface. As a result, the conductivity of the PP nonwovens became worse when the $CuSO_4$ concentration was too high.

TABLE II
Binding Energy Analysis of the Characteristic Peaks of the XPS Spectra

| | Functional groups | Binding energy (eV) | |
		Experimental data	Reported data
C1s	C—C/C—H	285.84	285.0
	C=O	288.39	288.0
O1s	Cu—O	530.06	530.0
	O—H	531.18	531
	O—C=O/C=O	532.21	532.20
Cu2p3	Cu	931.78	932.5
	Cu—O	933.9	933.6
	Cu—O	942.17	942

Figure 5 Effects of the reaction temperature on the surface resistance (vacuum degree = 30 Pa, reaction power = 50 W, pretreatment time = 1 min, $CuSO_4$ concentration = 20 g/L).

It could be concluded that the optimum $CuSO_4$ concentration was 20 g/L. This concentration was adopted in the following experiments.

Effect of the reaction temperature on the conductivity

The dependence of the conductivity on the reaction temperature is shown in Figure 5. The applied reaction temperatures were set as 33, 38, 43, 48, and 53°C, respectively.

Figure 5 reveals that the surface resistance decreased sharply as the reaction temperature rose to a certain extent. It decreased to a minimum value of 30.8 mΩ/sq as the reaction temperature reached 43°C and then increased gradually as the temperature continued to rise. At the same time, the reaction became more and more difficult when the temperature was over 50°C.

This was because the lower the reaction temperature was, the lower the solution activity was; this led to a slow deposition rate. Therefore, the reaction became considerably difficult at very low temperatures. On the contrary, the conductivity was improved with increasing reaction temperature to a certain extent. In this case, movements among particles in the reaction solution accelerated. Compact and collision among the particles and the substrates also sped up. Therefore, an erosion effect on the surface of the substrates was enhanced, and the catalysis active sites increased, which accelerated the copper deposition process. However, the velocity of the particles reached a limit with further increases in the reaction temperature because of the reflection effect among particles. The residence time was shortened because of the acceleration of the movements at high temperatures; this went against the deposition of

copper films and made them easy to peel off from the substrates and formed deposits of metal fragments. Therefore, the reaction was too difficult when the reaction temperature was beyond 50°C, as shown in Figure 5. The deposited copper film appeared to be thin and uneven; this affected the surface conductivity of the copper-coated PP nonwovens. Therefore, 43°C was the critical point of reaction temperature for this deposition process, which was applied in the following experiments.

Effect of the plasma power on the conductivity and adhesion

In the copper deposition process, sensitization, activation, and reduction were all chemical reactions taking place on the fiber surface. These reactions can be simply explained as follows: Sn reduced Sn^{4+} in the solution into Sn^{2+}, and Ag^+ was reduced into metal Ag grains by Sn^{2+} clinging on the PP nonwoven fiber. The reduced Ag grains first stuck on the fiber surface and then served as catalyzing centers for the subsequent copper deposition. Therefore, a highly wet and rough surface caused by the O_2 plasma pretreatment was greatly beneficial to the permeation of the reactive agent and resulted in more Ag grains[13] and copper deposition on the fiber surface. Furthermore, surface modification by plasma pretreatment had a significant influence upon the adhesion of the deposition to the PP nonwoven fibers.

In the plasma pretreatment, energy gains from the impingement of electrons in the electric field and gas molecules exciting the molecular separation could be described by the following equation:[14]

$$\frac{1}{2}mv^2 - \frac{1}{2}mv_0^2 = eU \tag{1}$$
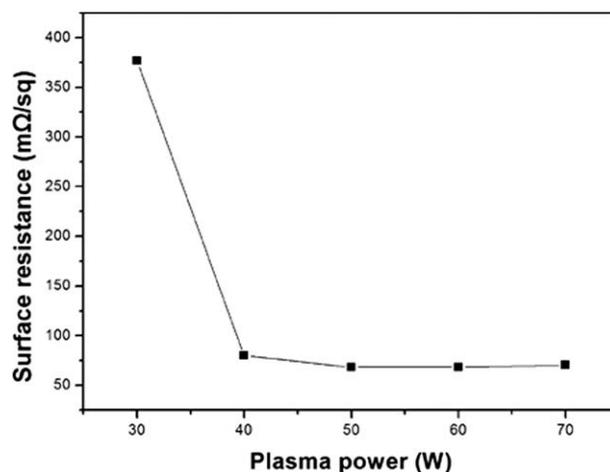
Figure 6 Effects of the plasma power on the conductivity (vacuum degree = 30 Pa, pretreatment time = 1 min, $CuSO_4$ concentration = 20 g/L, reaction temperature = 43°C).

where m is the electron mass, ν and ν_0 represent the velocities of the electrons before and after acceleration, and $U = ES$ represents the potential difference caused by the electrons as they pass distance S.

The obtaining energy ($\frac{1}{2}m\nu^2 - \frac{1}{2}m\nu_0^2$) varied directly as voltage U, which was in direct proportion to the plasma power. In other words, the obtaining energy, observed as the most significant parameter in the experiments, was in direct proportion to plasma power.

Effect of the plasma power on the conductivity

A series of reaction powers (30, 40, 50, 60, and 70 W) were applied to study their effect on the conductivity of the PP nonwovens after copper deposition.

Figure 6 indicates that the copper-deposited PP nonwovens exhibited a high surface resistance up to 377 mΩ/sq. However, as the plasma power was increased from 30 to 40 W, the surface resistance sharply decreased to 80.05 mΩ/sq and then showed a gentle drop; it tended to be stable at a value of about 65 mΩ/sq as the plasma power was increased from 40 to 70 W. It could be concluded that the conductivity of the PP nonwovens after copper deposition was enhanced as the plasma treatment power was increased.

It was etching that mainly worked on the PP nonwoven fibers when the O_2 plasma pretreatment was applied. This modification roughened the PP nonwoven fiber surface and directly affected the performance of copper deposition. The roughness effects were enhanced with the gradual increase in plasma power and facilitated the metallic deposition. However, it was observed that destruction of the substrates, such as crimping and brittleness, occurred if the plasma power was over 50 W. Therefore, a plasma treatment power of 50 W was used as the optimal parameter in the following experiments.

Deposition adhesion

Adhesion strength is an important parameter for characterizing coating deposition. To some extent, it reflected the binding fastness between the copper-deposited film and the PP nonwoven substrate. Thus, a series of plasma powers, namely, 30, 40, 50, 60, and 70 W, were selected to study the effect of O_2 plasma power on the adhesion strength of the copper deposition on the PP nonwovens, as described in Figure 7. In this study, the measured adhesion strength between the coatings and substrates was measured by peeling strength in the separation process.

As is shown in Figure 7, the adhesion strength was improved with increasing applied plasma power. As the plasma power was increased from 30
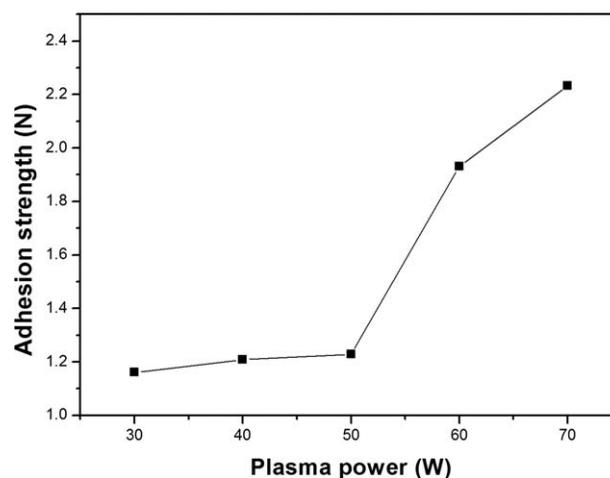
Figure 7 Effects of the plasma power on the adhesion strength.

to 50 W, the adhesion strength increased slightly. However, the adhesion strength significantly improved when the plasma power was increased from 50 to 70 W. This was because the surface roughness gradually increased with increasing plasma power. O_2 plasma treatment also introduced polar groups and active points on the PP nonwoven fibers. Hence, the adhesion strength of the metal film to the PP nonwoven fibers was significantly improved because of the chemical bonds or the van der Waals forces formed by the polar groups and active points.

The failure modes of the coated copper films on the PP nonwovens after the peel test could be classified as follows:[6] (1) fracture at the copper films; (2) fracture at the interface between the copper films and the PP nonwovens, and (3) fracture at the PP nonwovens. If the adhesion strength of the coated copper to the PP nonwovens was higher than the cohesive strength of the copper films and the cohesive strength of PP nonwovens, the failure mode of fracture at the copper films or the fracture at PP nonwovens were observed. In contrast, the failure mode of fracture at the interface between the copper films and the polymer fibers was observed. In this study, copper films with trace amounts of fibers on the tape surface were observed after the peel test; this demonstrated that the copper coatings after plasma treatment were stably and firmly bonded with the substrate PP nonwovens.

CONCLUSIONS

The functionalization of PP nonwovens by copper deposition was investigated in this study. It was found that surface resistances of the PP nonwoven as low as 30.8 mΩ/sq could be obtained by the electroless deposition of copper. The experimental

conditions also affected the surface conductivity of the copper-deposited nonwovens. This study proved that plasma pretreatment enhanced the adhesion of the copper film to the fibers and improved the deposition quality.

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