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Effects of Deposition Parameters of Electroless Copper Plating on Polyester Fabric

R. H. Guo, S. X. Jiang[1]*, C. W. M. Yuen[1], M. C. F. Ng[1], J. W. Lan, Y. L. Yeung[1], and S. J. Lin

College of Light Industry, Textile and Food Engineering, Sichuan University, Chengdu, China
[1]*Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*
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Abstract: Properties of electroless copper-plated polyester fabric mainly depend on the plating bath constituents/conditions. The nickel serves to catalyze the copper deposition when hypophosphite is used as a reducing agent. In this study, the effects of deposition parameters including additive $NiSO_4$ concentration and pH on microstructure and properties of the electroless copper plating on polyester fabric using hypophosphite as a reducing agent were investigated. The results show that at a higher $NiSO_4$ concentration, the copper content present in the coating decreases whereas the nickel content increases slightly. On the other hand, the copper content present in the coating increases, whereas the nickel content and phosphorus decreases with respect to the rise of pH. The morphology of the copper deposits show that the particle size increase with respect to the rise of $NiSO_4$ concentration and pH. The XRD patterns indicate that the copper-plated polyester fabrics are crystalline. In addition, there is a decrease in the surface resistance and an increase in the electromagnetic interference (EMI) shielding effectiveness (SE) with respect to the rise of Ni^{2+} concentration and pH of the solution as a result of gaining a greater weight in the deposits. The results suggest that the copper-plated polyester fabrics have a great potential application as an EMI shielding material.

Keywords: Electroless copper plating, Deposition parameters, Polyester fabric, Electromagnetic interference shielding

Introduction

Nowadays, the electromagnetic radiation is becoming the fourth public pollution in addition to the noise, water and air pollution. Electromagnetic interference is a well-known problem in commercial and scientific electronic instruments, antenna systems and military electronic devices. As is well known, electromagnetic interference shielding is in critical demand due to the increasing sensitivity and the interference between digital devices. As a result, human being is looking not only for the healthy electromagnetic environments, but also for daily works and particularly proper communications. It is obvious that there is a critical need for developing effective and practical EMI shielding materials and their potential applications in recent years. In general, conductive textiles which are coated with aluminum, copper, silver and nickel, are important types of material for preventing electromagnetic interference [1,2]. The currently developed metal coating techniques include metal foil and laminates, conductive paints and lacquers, sputter coating, vacuum deposition, flame and arc spraying, electroplating and electroless plating [3-7]. Among them, electroless plating is probably a preferred way to produce metal-coated textiles. The electroless deposition method uses a catalytic redox reaction between metal ions and dissolved reduction agent.

With regards to the high conductivity of copper, electroless copper plating is currently used to manufacture conductive fabrics. Electroless copper plating on fabrics has been studied by some researchers [8-10]. The conventional process of electroless copper deposition uses formaldehyde as the reducing agent [11]. Nevertheless, formaldehyde is listed as a carcinogen. Electroless copper plating using sodium hypophosphite as the reducing agent in place of formaldehyde is attractive because of its low pH, low cost, and relative safety, compared with high pH formaldehyde-based solutions [12]. However, the hypophosphite-based electroless copper plating process is complicated because copper is not a good catalyst for the oxidation of hypophosphite resulting in little or no plating on a pure copper surface. One approach to catalyze the oxidation of the reducing agent is to add nickel ions (or other metal ions) to the bath, resulting in a very small amount of co-deposited nickel in the copper deposit. The nickel serves to catalyze the oxidation of hypophosphite enabling continuous copper deposition [13]. However, effect of additive nickel ion concentration and pH on microstructure and properties of electroless copper-plated fabrics have not yet been reported in the open literature.

In this study, the effects of $NiSO_4$ concentration and pH of plating bath for the electroless copper plating on deposit compositions, surface morphology, and crystal structure are investigated. Surface resistance and EMI SE of the copper-plated polyester fabric were evaluated.

Experimental

Plain weave 100 % polyester fabric (47×40 counts/cm^2, 84 g/m^2) in white color were used as substrate. All chemicals were of analytical purity.

All of the fabric samples underwent pre-treatment before electroless plating. They were washed with 5 % non-ionic

*Corresponding author: tckinor@inet.polyu.edu.hk

Table 1. Bath composition and operating condition of electroless copper plating

Bath composition		Operating condition	
$CuSO_4 \cdot 5H_2O$ (g/*l*)	10		
$NiSO_4 \cdot 6H_2O$ (g/*l*)	0.8; 1.0; 1.5; 2.0; 2.5	pH	8.5, 9.0, 9.5, 10.0, 10.5
$NaH_2PO_2 \cdot H_2O$ (g/*l*)	30	Temperature (°C)	70
$Na_3C_6H_5O_7 \cdot 2H_2O$ (g/*l*)	20	Time (min)	20
H_3BO_3 (g/*l*)	30		

detergent at room temperature for 20 minutes and then rinsed thoroughly in deionized water. Surface sensitization was conducted by immersing the samples into an aqueous solution that contained 10 g/*l* stannous chloride and 40 m*l*/*l* hydrochloric acid (38 %) at 25 °C for 10 minutes. The samples were then rinsed in deionized water and activated by immersing them in a solution that contained 0.5 g/*l* palladium chloride and 20 m*l*/*l* hydrochloric acid (38 %) at 25 °C for 10 minutes. They were then rinsed in a large volume of deionized water for more than five minutes to prevent contamination of the plating bath. The samples were subsequently immersed in the electroless copper plating bath. The chemical compositions of this plating bath are given in Table 1.

In the post-treatment stage, the samples were rinsed in deionized water at 40 °C for 20 minutes and then dried in an oven at 60 °C. All of the copper-plated samples were conditioned in accordance with ASTM D1776-04 before measurement.

A field emission scanning electron microscope (SEM, JSM-6335F at 3.0 kV) was used to characterize the surface morphology of the Cu deposits, and their chemical composition was determined via an energy dispersive X-ray (EDX) attached to the SEM. The crystal structure of the deposits was investigated using X-ray diffraction (XRD, Cu Kα radiation and a graphite filter at 40 kV and 40 mA). Surface resistance (Rs) was measured by the four-probe method described in ASTM F 390. Rs is considered to be the resistance of a square sample, and units of Rs are commonly expressed as ohms per square or Ω/sq. EMI shielding effectiveness (SE) was obtained according to ASTM D 4935-99 by using a vector network analyzer (Agilent-E8363A) equipped with a synthesized frequency source and a scattering parameter (S-parameter) test set over a frequency range of 2 to 18 GHz.

Results and Discussion

Deposit Composition and Weight

The deposit composition strongly depends on the deposition conditions. Copper is the dominant component within the copper coating. The composition of the coatings suggests that only a small quantity of nickel and phosphorus is formed

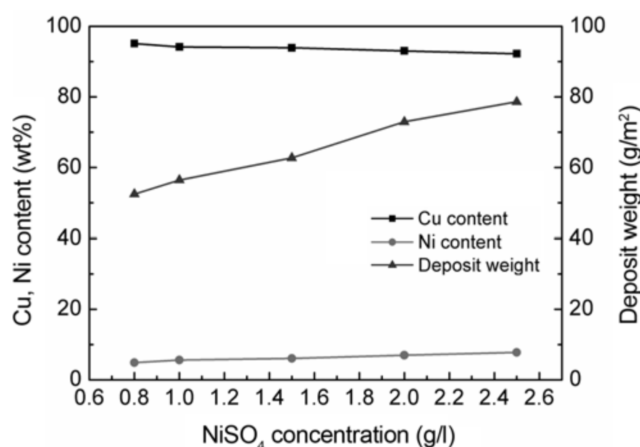
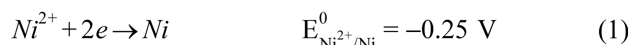


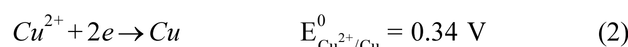
Figure 1. Composition and weight of copper deposits on polyester fabric with different $NiSO_4$ concentration.

within the bulk of the coatings. The deposit of the electroless copper plating using hypophosphite as the reducing agent is actually Cu-Ni-P alloy [12].

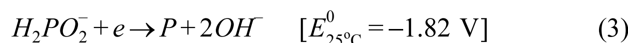
The chemical composition and weight of the electroless copper deposits with different nickel ion concentrations in the alkaline plating bath is shown in Figure 1. The deposit layers with different copper contents ranging from 95.13 % to 92.24 % are obtained. The higher copper content in the deposits is believed to be due to the higher reduction potential of copper than that of the nickel and phosphorus. According to the electrochemistry, the standard reduction potential of copper, nickel, and hypophosphite in basic solution are shown as follows [14]:



$$Ni^{2+} + 2e \rightarrow Ni \qquad E^0_{Ni^{2+}/Ni} = -0.25\ V \tag{1}$$



$$Cu^{2+} + 2e \rightarrow Cu \qquad E^0_{Cu^{2+}/Cu} = 0.34\ V \tag{2}$$



$$H_2PO_2^- + e \rightarrow P + 2OH^- \qquad [E^0_{25^\circ C} = -1.82\ V] \tag{3}$$

Therefore, both Cu^{2+} and Ni^{2+} can be reduced to copper and nickel by hypophosphite in alkaline solution, and the reduced trend of Cu^{2+} is higher than that of Ni^{2+}. In other words, Cu^{2+} can obtain electrons from $H_2PO_2^-$ more easily than Ni^{2+}. On the other hand, phosphorus is not observed in the deposits. The phenomenon is explained by the fact that the reduction potential of phosphorus is relatively lower than that of copper and nickel, thereby inhibiting the reduction of hypophosphite.

When the nickel sulfate concentration is increased in the solution, the copper content in the coating will decrease whereas the amount of nickel will increase slightly. The copper content decreases from 95.13 % to 92.24 % but reversely the nickel content in the deposits increases from 4.87 % to 7.76 % as the mol ratio of $NiSO_4/(CuSO_4+NiSO_4)$ in the plating bath increases from 0.076 to 0.237. Table 2

Table 2. The mol ratio of Ni/(Cu+Ni) in films deposited in various plating baths

	1	2	3	4	5
Mol ratio of Ni/(Cu+Ni) in plating bath	0.076	0.095	0.143	0.190	0.237
Mol ratio of Ni/(Cu+Ni) in the coatings	0.051	0.060	0.065	0.074	0.084

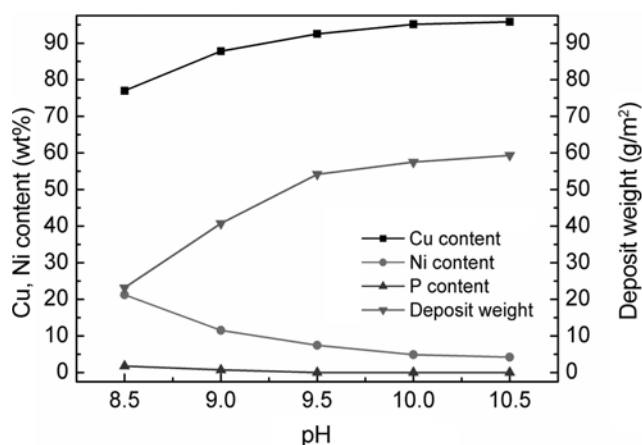


Figure 2. Composition and weight of copper deposits on polyester fabric at different pH.

shows the mol ratio of Ni/(Cu+Ni) in the coating and in the plating bath concerned. The mol ratio of Ni/(Cu+Ni) in the coating is smaller than that in the plating bath implying that the Cu^{2+} ions are easier to be reduced to form atoms and then attach to the film surface than the Ni^{2+} ion in the plating baths. In addition, the weight of the copper deposits increases with increasing $NiSO_4$ concentration as shown in Figure 1.

Figure 2 shows the deposit composition of the electroless copper-plated polyester fabrics at different pH. The percentage of copper in the deposits increases from 76.99 % to 95.83 % when the pH of the solution is raised from 8.5 to 10.5. On the contrary, the relative amount of nickel decreases from 21.26 % to 4.17 % and the percent of phosphorus also decreases from 1.76 % to 0.7 % when pH is changed from 8.5 to 9.0. However, phosphorus is not observed when pH is at 9.5, 10.0 and 10.5.

In general, the reducing ability of sodium hypophosphite increases with respect to the rise of pH. This is due to the fact that higher pH can help generate more hydrogen followed by more nickel and copper in the coating as described in equations (4), (5) and (6) below [15]:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H_{ad} \quad (4)$$

$$Ni^{2+} + 2H_{ad} \rightarrow Ni + 2H^+ \quad (5)$$

$$Cu^{2+} + 2H_{ad} \rightarrow Cu + 2H^+ \quad (6)$$

With increasing pH, the secondary reaction usually occurred between the hypophosphite and hydrogen to form the elemental phosphorus is inhibited as shown in equation (7).

$$H_2PO_2^- + H_{ad} \rightarrow P + H_2O + OH^- \quad (7)$$

At higher pH, the reaction shown in equation (4) is facilitated to proceed forward by decreasing the concentration of the hypophosphite ions in the solution. Consequently, the amount of phosphorus present in the deposit decreases. The interaction between Cu^{2+} and $H_2PO_2^-$ is more favored at higher pH than that of lower pH. However, higher pH of the solution is not in favor of the reduction of Ni^{2+}. From Figure 2, it can be seen that the weight of the copper deposits increases with the rise of pH.

Surface Morphology

The surface morphology of the copper deposits was investigated using SEM. The SEM micrographs of original and the copper-plated polyester fibers with different nickel ion concentrations are shown in Figure 3. In comparison with the original polyester fiber in Figure 3(a), the surface of the polyester fiber is apparently completely covered with an copper coating as shown in Figure 3(b)-(e). It was also found that the copper deposits are uniformly distributed and dense on the surface of the polyester fibers. It is obvious that the particles size increases at higher nickel ions concentration. At the same time, it is found that the deposited film is composed of loosely stacked copper with uniform distribution. With more careful observation, it can be seen that some particles aggregate together to form larger granules. When the concentration of $NiSO_4$ is 0.8 g/*l*, the surface of copper sheet is in the form of granular structure but the size of the granules composing of the aggregates is in the range of 100-150 nm as shown in Figure 3(b). However, when the concentration of $NiSO_4$ is increased to 1.0 g/*l*, more granules with the average size of 150-200 nm are formed as shown in Figure 3(c). When the concentration is further increased to 1.5 g/*l* and 2.0 g/*l* respectively, it is found that the average size of the granules becomes even larger but the number of the porous structure decreases accordingly as shown in Figures 3(d) and (e). The result indicates that the copper crystal grains with higher $NiSO_4$ concentration are bigger than those with lower $NiSO_4$ concentration. This suggests that the effect of $NiSO_4$ concentration on the growth of copper crystal is positive. In addition, higher $NiSO_4$ concentration possibly can accelerate the growth of copper crystal growth but inhibit the nucleation of copper crystal.

Figure 4 shows the SEM images of the copper-plated

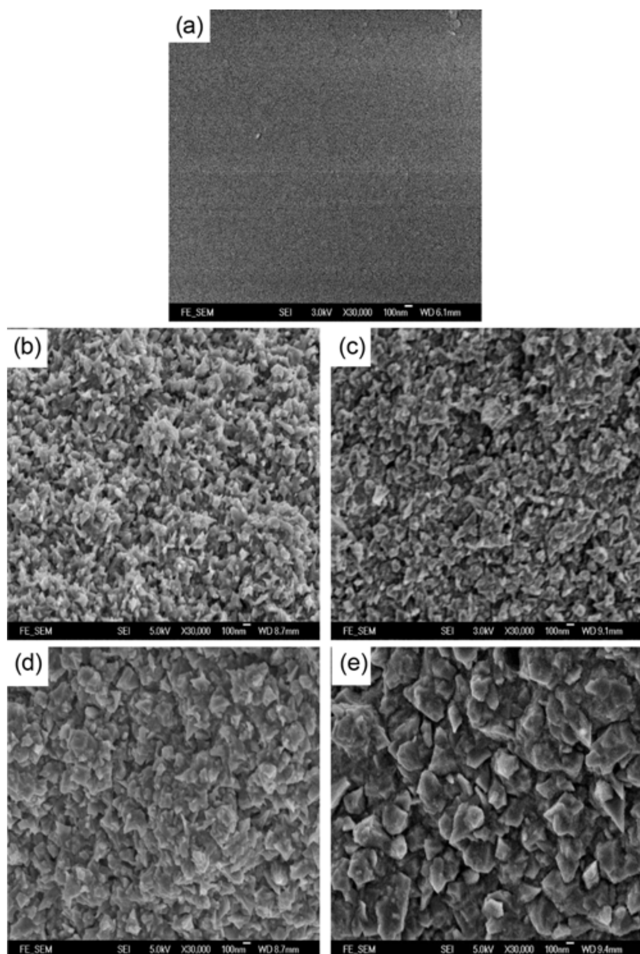


Figure 3. SEM micrographs of (a) orginal polyester, and copper-plated polyester fibers treated with different $NiSO_4$ concentrations: (b) 0.8 g/*l*, (c) 1.0 g/*l*, (d) 1.5 g/*l,* and (e) 2.0 g/*l.*

polyester fibers obtained from different pH of the plating solution. The SEM micrographs of copper deposits reveal that the deposits are composed of granules with different shapes and sizes. The surface morphology of the copper deposits largely depends on the bath pH. In the copper bath at pH 8.5, fine nano-particles formed on the polyester fibers are arranged randomly. As the bath pH is increased to 9.0, their shape gradually transforms from a nano-particle to a nano-block shape. It is obvious that particles size increases with the respect to the rise of pH in the plating solution. The deposition behavior of the electroless copper deposit can be described in the following steps. In the sensitization process, there are many nano-sized tin particles deposited on the surface of the polyester fiber substrate. During the activation process, the palladium particles with a larger size and less quantity than tin emerge on the surface of substrate. In the electroless plating process, the copper particles can deposit at the sites not only near palladium, but also at a distance from the palladium particles. The copper particles consist of

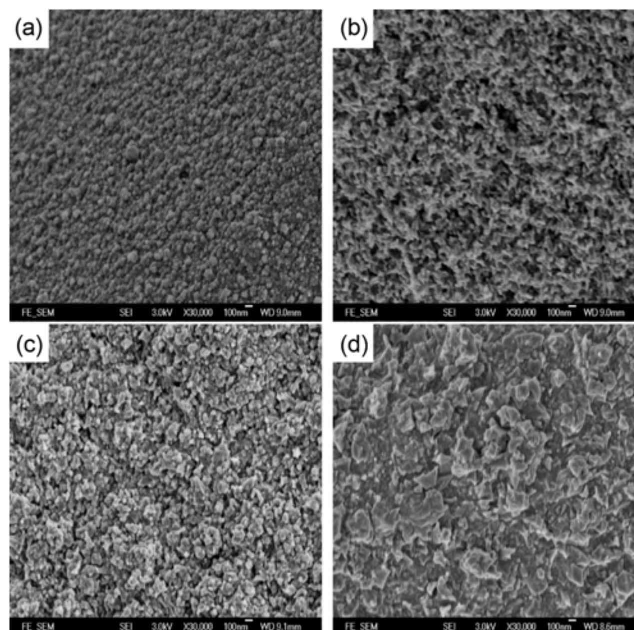


Figure 4. SEM micrographs of the copper-plated polyester fibers treated in the bath at different pH: (a) 8.5, (b) 9.0, (c) 9.5, and (d) 10.

tiny grains and their shape is roughly spherical in the initial stage. When the copper particles grow large enough to touch each other in the horizontal direction, they will merge to form larger particles and become nano-blocks in shape. This is probably due to the hindrance of hydrogen and bubbles. As a result, the copper deposit generally contains a bottom layer of small particles beneath the layer of larger grains.

Crystal Structure

Figures 5 and 6 show the XRD patterns of the copper-plated polyester fabrics with different nickel ion concentrations and pH of the plating bath respectively. The four major strong characteristic peaks of the copper-plated polyester samples at 2θ=43.4 °, 50.3 °, 74.2 ° and 90.1 ° correspond to the crystal faces of (111), (200), (220) and (311) of copper respectively. The XRD patterns identified by the PDF card of the JADE-SCAN software reveal that the deposited copper film exhibits a characteristic face-centered cubic crystalline structure, implying that the copper-plated polyester fabrics have a perfect conductivity property. The characteristic peaks of nickel are not observed in the XRD diagram probably due to the distribution of Ni in the coatings. In addition, it is worth noting that the copper films formed under different conditions were very pure without any detectable impurity such as CuO, Cu_2O or NiO. This is probably due to the fact that higher $NiSO_4$ concentration and pH can make the solubility of O_2 gas decrease in the bath [16], resulting in the generation of higher driving force to enhance the reduction of copper and nickel. As a result, the formation of

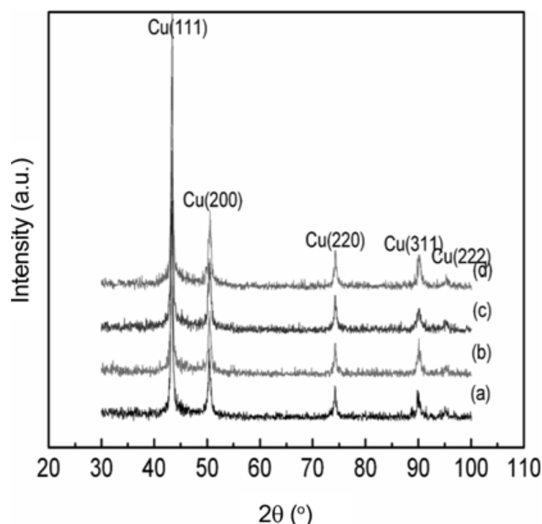


Figure 5. XRD patterns of the copper-plated fabrics with different $NiSO_4$ concentrations; (a) 0.8 g/*l*, (b) 1.0 g/*l*, (c) 1.5 g/*l,* and (d) 2.0 g/*l.*

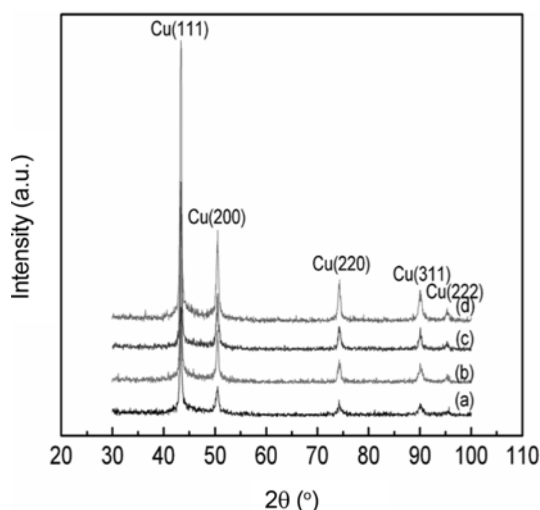


Figure 6. XRD patterns of the copper-plated fabrics at different pH; (a) 8.5, (b) 9.0, (c) 9.5, and (d) 10.

copper oxide and nickel oxide is prevented. High Cu (111)/ Cu (200) ratio is observed in the copper deposits, indicating that the copper film manifests the preferred (111) orientation. The copper film with a higher (111) texture is preferred due to its higher reliability against electro-migration and lower electrical resistance [17]. The ratio of Cu (111)/ Cu (200) is 3.06 for 0.8 g/*l* as shown in Figure 5(a). Figures 5(b) and (c) show that the Cu (111)/Cu (200) ratio rises to 3.37, 3.48 and 3.56 as the $NiSO_4$ concentration is increased to 1.0 g/*l*, 1.5 g/*l* and 2.0 g/*l* respectively. The ratio of Cu (111)/Cu (200) is 2.93 at pH 8.5 as shown in Figure 6(a). Figures 6(b)-(d) show that the Cu (111)/Cu (200) ratio rises to 3.07, 3.24 and 3.60 as the pH is increased to 9.0, 9.5 and 10.0 respectively. The intensity of the copper peaks increases with respect to the rise of the $NiSO_4$ concentration and pH, which is due to the growth of the copper particles. The crystallinity of the copper-plated polyester fabrics is also strengthened with increasing $NiSO_4$ concentration and pH.

Based on the XRD results, the crystal size of the coatings can be determined from the broadening of the diffraction peak from the (111) planes by employing the Scherrer formula as expressed by equation (8) [18]:

$$D = \frac{n\lambda}{B\cos\theta} \tag{8}$$

where D is the crystal size, λ is the X-ray wavelength corresponding to Cu Kα radiation (0.154056 nm), θ is the diffraction angle; B is the full width half maximum (FWHM) of the diffraction peak at 2θ, n is the Scherrer constant as 0.89.

According to the Scherrer equation, the average sizes of copper particles are 26.68 nm, 27.85 nm, 30.70 nm and 32.57 nm with respect to the Cu (111) main peak for 0.8 g/*l*, 1.0 g/*l*, 1.5 g/*l* and 2.0 g/*l* $NiSO_4$ respectively. Furthermore, the average sizes of copper particles are 21.42 nm, 25.41 nm, 26.36 nm and 28.01 nm with respect to the Cu (111) main peak for the pH of 8.5, 9.0, 9.5 and 10.0 respectively. Therefore, the results indicate that the particles grow at higher $NiSO_4$ concentration and pH.

Surface Resistance

The surface resistance of the copper-plated fabrics with different $NiSO_4$ concentrations and pH of the plating bath is shown in Figures 7 and 8 respectively. It is observed that the surface resistance of the copper deposits decreases with respect to the increase in $NiSO_4$ concentration and pH. Although nickel content in copper deposits increases, the decrease in resistance is mostly attributed to the increase in the weight of copper deposits, particle size and crystallinity

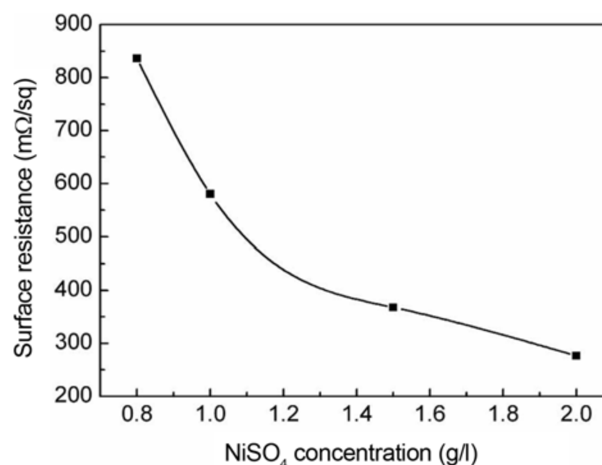


Figure 7. Surface resistance of the copper-plated polyester fabrics with different $NiSO_4$ concentrations.

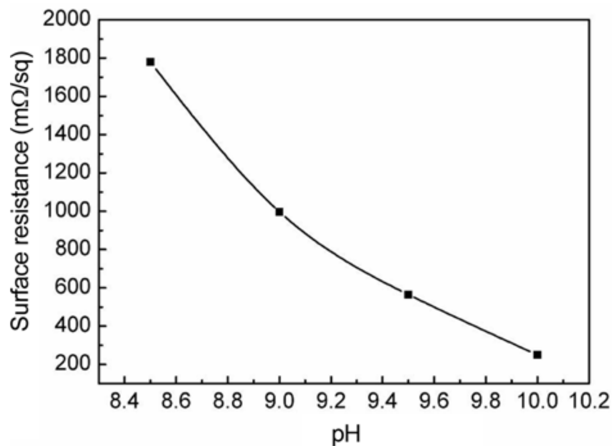


Figure 8. Surface resistance of the copper-plated polyester fabrics at different pH.

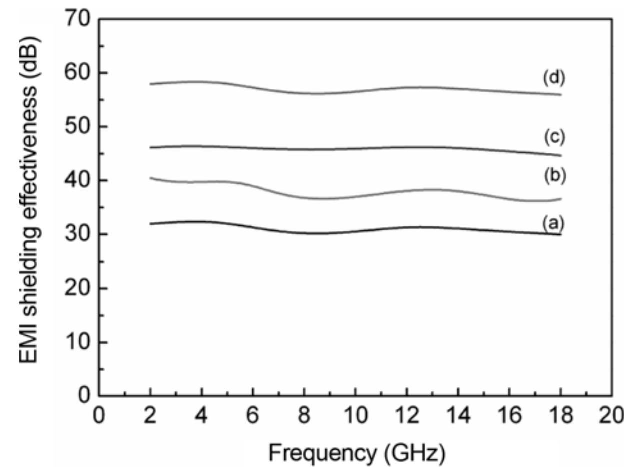


Figure 10. EMI shielding effectiveness of the copper-plated fabrics at different pH; (a) 8.5, (b) 9.0, (c) 9.5, and (d) 10.

in the present study. On the other hand, the reduction of surface resistance at higher pH is due to the increase in the weight of copper deposits, decrease of in the nickel content, the increasing particle size and crystallinity in the deposits. The result also indicates that the surface resistance of the electroless copper deposits is higher than that of the bulk copper as measured by a four-point probe because the nickel atoms co-exist in the copper coatings. This can be explained by the fact that nickel has a high electrical resistivity, and the nickel atoms in the copper lattice increase the number of crystal defects in the copper deposits. The resistance rate of the two metals concerned at 25 ^{o}C is as follows: Cu=1.750 $\times 10^{-8}$ Ω m; Ni=6.84$\times 10^{-8}$ Ω m [19].

EMI Shielding Effectiveness

Figures 9 and 10 show the EMI SE of the copper-plated fabrics with different concentrations of $NiSO_4$ and pH respectively. The EMI SE of the copper-plated polyester fabrics ranges from 30 to 60 dB at the frequency of 2 GHz to 18 GHz with different $NiSO_4$ concentrations and pH. The EMI SE increases with respect to higher $NiSO_4$ concentrations and pH due to increased quantity of copper deposits, large grain size and higher crystallinity in the deposits. The result shows that the plated polyester fabric has good EMI shielding effectiveness.

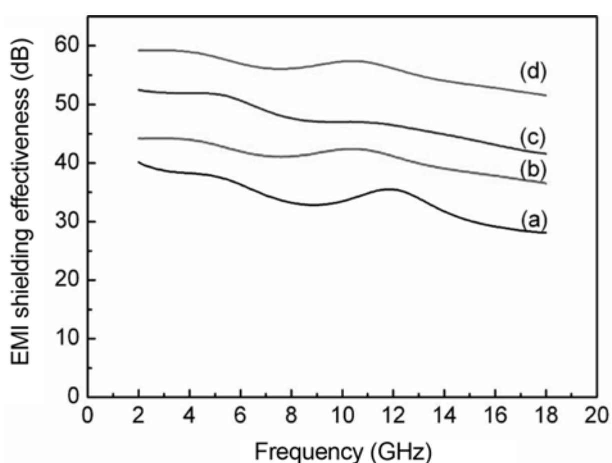


Figure 9. EMI shielding effectiveness of the copper-plated fabrics with different $NiSO_4$ concentrations; (a) 0.8 g/*l*, (b) 1.0 g/*l*, (c) 1.5 g/*l*, and (d) 2.0 g/*l*.

Conclusion

Effect of deposition parameters including $NiSO_4$ concentration and pH on microstructure and properties of electroless copper-plated polyester fabric using hypophosphite as a reducing agent was investigated. The results show that at a higher $NiSO_4$ concentration, the copper content present in the coating decreases. On the contrary, the nickel content increases slightly but the phosphorus is not observed. On the other hand, the copper content present in the coating increases, whereas the nickel content and phosphorus decreases with respect to the rise of pH. The surface morphology of the copper deposits show that the particle size increases with respect to the rise of $NiSO_4$ concentration and pH. The XRD patterns indicate that the copper-plated polyester fabrics are crystalline. In addition, there is a decrease in the surface resistance and an increase in the EMI SE with respect to the rise of Ni^{2+} concentration and pH of the solution as a result of gaining a greater weight in the deposits. The results suggest that the copper-plated polyester fabrics have a great potential application as an EMI shielding material.

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References

1. A. Schwarz, J. Hakuzimana, A. Kaczynska, J. Banaszczyk, P. Westbroek, E. McAdams, G. Moody, Y. Chronis, G. Priniotakis, G. D. Mey, D. Tseles, and L. V. Langenhove, *Surf. Coat. Technol.*, **204**, 1412 (2010).
2. X. Q. Liu, H. X. Chang, Y. Li, W. T. S. Huck, and Z. J. Zheng, *ACS Appl. Mater. Interface*, **2**, 529 (2010)
3. S. X. Jiang, W. F. Qin, R. H. Guo, and L. Zhang, *Surf. Coat. Technol.,* **204**, 3662 (2010).
4. M. Z. Balbag and S. Pat, *J. Plast. Film Sheet.*, **27**, 209 (2011).
5. J. Park, H. Fujita, and B. Kim, *Sensor Actuat. A-Phys.*, **168**, 105 (2011).
6. R. H. Guo, S. Q. Jiang, C. W. M. Yuen, and M. C. F. Ng, *J. Appl. Electrochem.*, **39**, 907 (2009).
7. S. Q. Jiang and R. H. Guo, *Fiber. Polym.*, **9**, 755 (2008).
8. Y. X. Lu, Q. Liang, and L. L. Xue, *Appl. Surf. Sci.*, **258**, 4782 (2012).
9. R. H. Guo, S. Q. Jiang, C. W. M. Yuen, and M. C. F. Ng, *J. Mater. Sci.: Mater. Electron*., **20**, 33 (2009).
10. A. Garcia, J. Polesel-Maris, P. Viel, S. Palacin, and T. Berthelot, *Adv. Funct. Mater.*, **21**, 2096 (2011).
11. X. Wang, N. Li, Z. F. Yang, and Z. L. Wang, *J. Electrochem. Soc.*, **157**, D500 (2010).
12. X. P. Gan, K. C. Zhou, W. B. Hu, and D. Zhang, *Surf. Coat. Technol.,* **206**, 3405 (2012).
13. S. Z. Chu, M. Sakairi, and H. Takahashi, *J. Electrochem. Soc.,* **147**, 1423 (2000).
14. C. J. Chen and K. L. Lin, *J. Electrochem. Soc.,* **146**, 137 (1999).
15. H. G. Ying, M. Yan, T. Y. Ma, J. M. Wu, and L. Q. Yu, *Surf. Coat. Technol.*, **202**, 217 (2007).
16. J. J. Kim, S. H. Cha, and Y. S. Lee, *Jpn. J. Appl. Phys.*, **42**, L953 (2003).
17. Y. Y. S. Diamand, *Electrochem. Solid ST.,* **3**, 279 (2000).
18. B. E. Warren, "X-ray Diffraction", Dover, New York, 1990.
19. Y. Gao, L. Huang, Z. J. Zheng, H. Li, and M. Zhu, *Appl. Surf. Sci*., **253**, 9470 (2007).