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Metallization of Polyester Fabric by Autocatalytic Copper Plating Process Using Glyoxylic Acid as a Reducing Agent

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Abstract: In this study, metallization of polyester fabric was studied by autocatalytic copper plating using glyoxylic acid as a reducing agent. Surface morphology, composition, and crystal structure of copper coating on polyester fabrics after electroless deposition were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and X-ray diffraction (XRD), respectively. Surface resistance and electromagnetic interference shielding effectiveness (EMI SE) of copper plated polyester fabric were evaluated. It is found that the surface resistance was 128 mΩ/sq and EMI SE arrives at 40-50 dB at the frequency of 6 GHz to 18 GHz as the concentration of copper sulfate was 11 g/*l*.

Keywords: Glyoxalic acid, Electroless, Copper, Polyester, Environment-friendly

Introduction

Metallized fabrics, which are coated with aluminum, copper, silver, and nickel, are important kinds of materials for preventing electromagnetic interference, absorbing radiation of electromagnetic wave, and reflecting ultraviolet rays and infrared. Metallized fabrics show great potentials in the military, commercial, and industrial areas [1-4]. Methods for metallizing include vapor deposition [5], sputtering [6], electrodeposition [7], and electroless deposition [8-10]. Among them, electroless plating is probably a preferred method to produce metallized fabrics. Electroless deposition method employs a catalytic redox reaction between metal ions and reducing agent dissolved in plating solution. With its remarkable advantages such as low cost and easy formation of a continuous and uniform coating on the surface of textiles with complex shapes, electroless plating can be performed at any step of textile production such as yarn, stock, fabric, or clothing [11].

Electroless copper deposition technology has rapidly advanced in recent years including widespread application in areas such as through-hole plating in printed circuit boards, decorative plating of household utensils, and automotive industry, electromagnetic interference shielding of electronic components, conductive traces in electronic interconnection devices and integrated circuit manufacturing, and conductive and decorative plating of textiles [12-16]. Electroless plating has been frequently used for copper deposition on polyester fabric [17-19]. However, in traditional electroless copper plating on polyester fabric, formaldehyde has been used as the reducing agent with its strong reduction ability and cheap price. However, formaldehyde is harmful to humans and environment. Therefore, the processes of traditional electroless copper deposition technology are not environmentally friendly. When the society pays more and more attention on environmental protection, formaldehyde must be substituted by other reducing agents [20,21]. As an alternative, glyoxylic acid is a good choice with its higher deposition rate and less environmental pollution. In addition, electroless plating bath is more stable with glyoxylic acid as a reducing agent [22,23]. However, no study has been reported on electroless copper plating on polyester fabric with glyoxylic acid as a reducing agent.

In this study, an efficient and environmental-friendly method was developed to deposit copper coating on the polyester fabric by autocatalytic copper plating using glyoxylic acid as reducing agent. Effect of copper sulfate in plating bath on microstructure and properties of copper plated polyester fabrics was investigated. Copper plated polyester fabrics were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), surface resistance, and EMI SE.

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Experimental

Material

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

Electroless Copper Plating

Polyester fabrics were cleaned with deionized water. The fabrics were immersed into 5 g/*l* copper sulfate solution for 10 min, and then they were placed into 5 g/*l* sodium borohydride solution for 10 min. After that, the fabrics were impregnated into copper plating solution. The solution for copper plating was prepared by EDTA, potassium ferrocyanide, deionized water, glyoxylic acid, and different concentration of copper sulfate. Sodium hydroxide was used to adjust pH of the plating solution. After copper plating, the fabrics were rinsed with deionized water and dried at 70 °C.

Characterization

The electronic balance (Hang Ping FA2004N) was used to weigh the fabrics before and after copper plating. Deposition rate was calculated by the following equation.

$$d = \frac{m_2 - m_1}{S \times t} \tag{1}$$

where d is deposition rate, m_1 and m_2 are the weight of fabrics before and after copper plating, respectively, S is area of the fabrics, and t is time of copper plating.

SEM images were obtained using a TM-3000 Tabletop Microscope with various magnifications to study the surface morphology of the polyester fibers and copper plated polyester fibers. Elemental composition of the copper plated fabrics was obtained by EDX detector on a JEOL JSM6490. Crystal structure of copper deposits on the polyester fabrics was characterized by a D8 Discover X-ray diffractometer.

Surface resistance of the copper coated polyester fabrics was measured by an RTS-9 Dual Electric Logging Four Point Probe Tester, produced by Guangzhou Four-point Probe Technology Company. EMI SE was evaluated by an Agilent-E8368A network analyzer produced by Agilent Scientific and Technical Company.

Results and Discussion

Deposition Rate

Influence of concentration of $CuSO_4$ on deposition rate is illustrated in Figure 1. The result shows that deposition rate obviously increases with the rise of $CuSO_4$ concentration. The main reason is that the increase of the concentration of copper ions promotes the mass transfer of the electrode surface and accelerates the rate of electron transfer. When

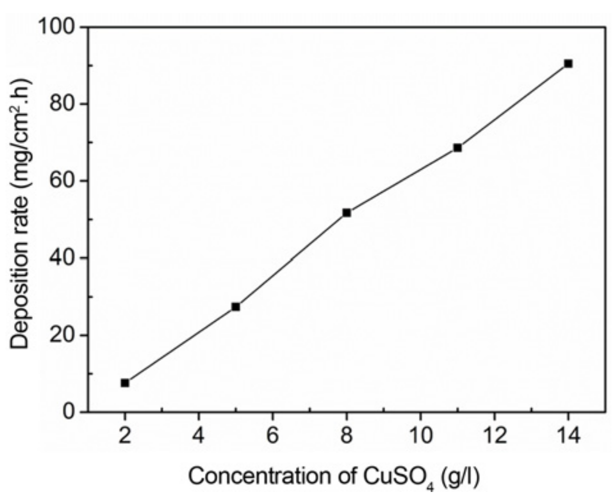

Figure 1. Influence of concentration of $CuSO_4$ in plating solution on the deposition rate.

the concentration of copper ions is low, the deposition rate is low and the reduction process of Cu^{2+} into Cu must be through the middle product Cu^+. In this study, when the concentration of Cu^{2+} ions continued to raise, the deposition rate significantly declines because the stability of solution bath decreases, minimizing the effect of complexing agents, leading to adverse reaction in solution, which results in electrolyte decomposition.

So far, there are four main theories for the mechanism of deposition in the kinetics of the electroless plating, atomic hydrogen mechanism, hydride transfer mechanism, hydroxy-metal ion coordination mechanism, and electrochemical mechanism. Electrochemical mechanism is based on the mixed potential theory, which considers that the anodic process and the cathodic process are relatively independent. The deposition rate of electroless plating can be explained by the mixed potential theory. In this study, following are the main reactions during eletroless copper plating.

Anodic reaction:

$$2CHOCOOH + 4OH^- = 2HC_2O_4^- + 2H_2O + H_2\uparrow + 2e \tag{2}$$

Cathodic reaction:

$$Cu\,(EDTA)^{2-} + 2e = Cu + EDTA^{4-} \tag{3}$$

Overall reaction:

$$Cu\,(EDTA)^{2-} + 2CHOCOOH + 4OH^- = Cu + 2HC_2O_4^- + 2H_2O + H_2\uparrow + EDTA^{4-} \tag{4}$$

Possible side reaction:

$$2Cu^{2+} + CHOCOOH + 5OH^- = Cu_2O\downarrow + HC_2O_4^- + 3H_2O \tag{5}$$

$$2CHOCOOH + 2OH^- = C_2O_4^{2-} + 2HOCH_2COOH + H_2O \tag{6}$$

$$Cu_2O + H_2O = Cu\downarrow + Cu^{2+} + 2OH^- \tag{7}$$

Surface Morphology of Copper Plated Fibers

Surface morphology of original and the copper plated polyester fibers with different concentration of copper sulfate are shown in Figure 2. As seen in Figure 2(a), polyester fibers are cylindrical and the surface of fiber is smooth. Figure 2(b)-(f) show surface morphology of copper deposits on polyester fibers with different concentration of copper sulfate. The polyester fibers are completely covered with copper particles. Size of copper particles increases with the rise of concentration of copper sulfate. The surface of polyester fibers are uniformly covered with copper particles and particle size of copper is small when copper sulfate concentration is 2 g/*l* (Figure 2(b)). The size of copper particles becomes bigger when copper sulfate concentration is 5 g/*l* (Figure 2(c)). When the concentration is 8 g/*l* (Figure 2(d)), the copper grain on fiber becomes larger and the grain gathers obviously together, however, the distribution and the

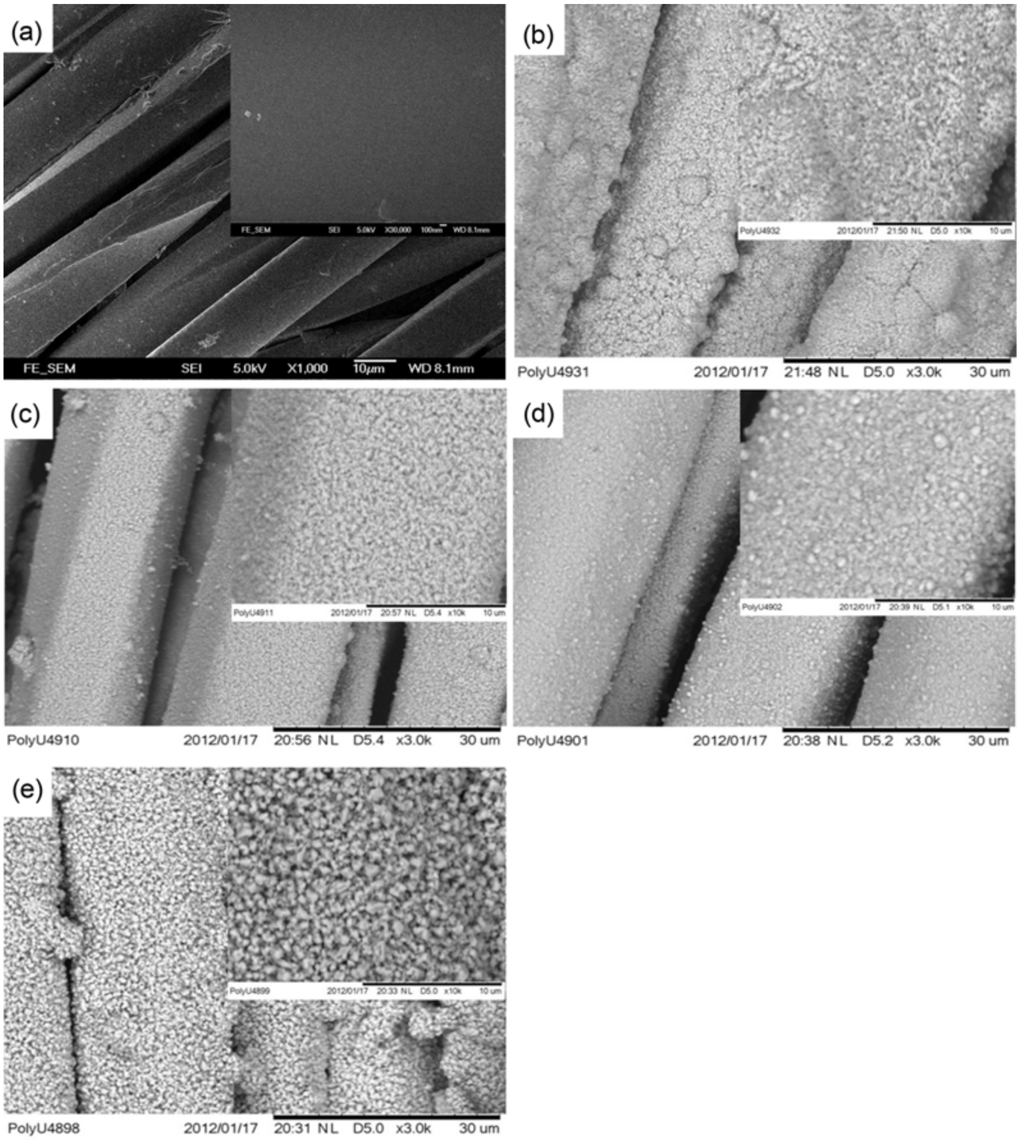

Figure 2. SEM of (a) original polyester fibers and copper plated polyester fibers with different concentration of copper sulfate (b) 2 g/*l*, (c) 5 g/*l*, (d) 8 g/*l*, and (e) 11 g/*l*.

size of copper grain are uneven. When copper sulfate concentration is 11 g/*l* (Figure 2(e)), the copper grain becomes bigger and the distribution is uniform. The reason is that the copper deposition rate improves and the copper deposits rapidly grow with the increase of the concentration of copper sulfate.

Chemical Composition of Copper Plated Fabrics

The composition of deposits was tested by an energy dispersive X-ray detector. Figure 3 shows EDX spectrum of the copper plated polyester fabrics where the concentration of copper sulfate is 11 g/*l*. It is obvious that there are three characteristic peaks of copper and one characteristic peak of oxygen. From the data of EDX spectrum, there are only

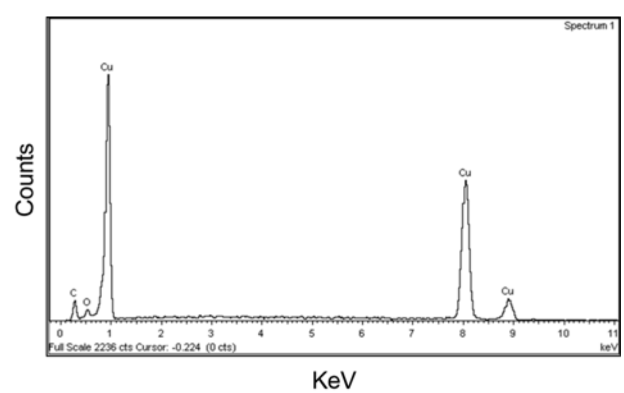

Figure 3. EDX image of copper plated polyester fabric.

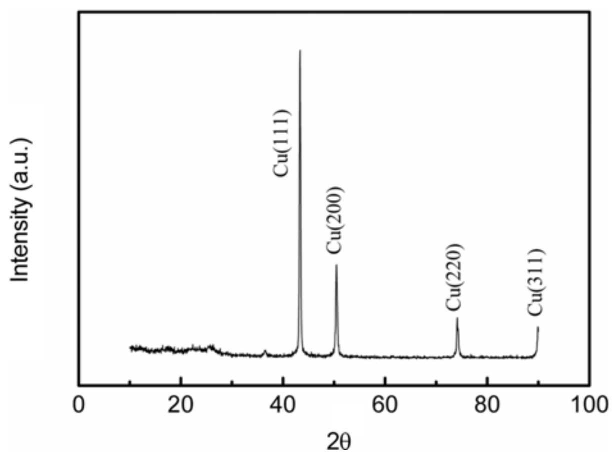

Figure 4. XRD pattern of copper plated polyester fabric.

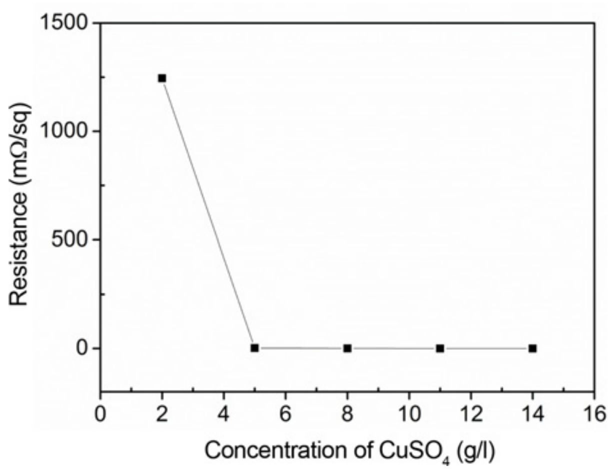

Figure 5. Surface resistance of copper plated polyester fibers with different concentrations of copper sulfate.

copper (95.5 %) and oxygen (4.5 %) elements in the deposition, besides carbon and hydrogen elements. It indicates that the coating is mainly composed of Cu. Therefore, metallic copper is deposited on the fabric after the copper plating.

Crystal Structure

Figure 4 presents the X-ray diffraction (XRD) pattern of the electroless plating copper on polyester fabric. From the pattern, the sharp peaks that appear at 2θ=43^o, 50^o, 74^o, and 90^o represent crystals planes of cubic metallic copper (111), (200), (220), and (311), respectively. The result confirms the existence of copper in the form of Cu crystals, which is in a very good agreement with the standard of metallic copper peaks (JCPDS Card No.85_1326). The diffraction peaks of copper oxide are not detected in the XRD pattern. The result shows that the plated copper is pure and there is no impurity Cu_2O under this process conditions. The peak (111) is sharp and the full width at half maximum (FWHM) is small. The result suggests that copper deposit has good crystallization.

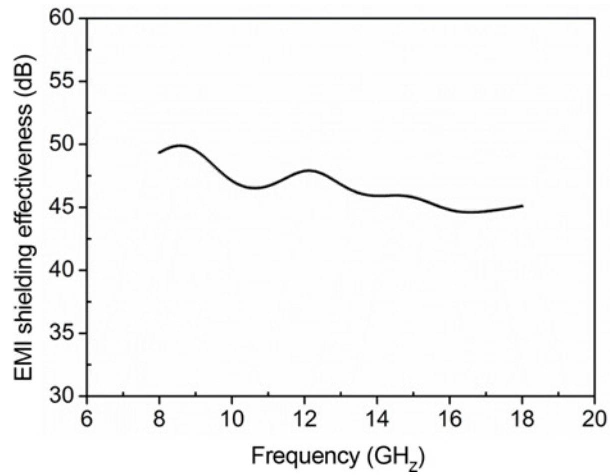

Figure 6. EMI SE of copper plated polyester fabric.

Surface Resistances

Surface resistance of copper plated polyester fabric with different concentration of copper sulfate is illustrated in Figure 5. Surface resistance becomes lower when the concentration of copper ions in the copper plating solution is increased. The surface resistance is related to the amount of copper deposits on polyester fabric. It can be explained that the copper deposits on polyester fabric resulting from higher deposition rate with the higher concentration of copper sulfate as shown in Figure 1 are thicker. The surface resistance is 128 mΩ/sq when the concentration of copper sulfate arrives at 11 g/*l*.

EMI Shielding Effectiveness

EMI SE of the copper plated polyester fabric obtained when the concentration of copper sulfate is 11 g/*l* is shown in Figure 6. EMI SE of the copper plated fabric ranges from 40 to 50 dB at the frequency of 6 GHz to 18 GHz. The copper plated polyester fabric shows high EMI SE mainly due to its good electric conductivity.

Conclusion

Copper was deposited on polyester fabric using glyoxylic acid as a reducing agent with different concentrations of copper sulfate in the solution by electroless plating. The deposition rate obviously increased with the rise of the concentration of copper ions in the bath. Copper deposits on polyester fabrics mainly contained metallic copper with good crystallinity. Surface resistance became lower when the concentration of copper ions in the plating solution was increased. The surface resistance is 128 mΩ/sq when the concentration of copper sulfate arrives at 11 g/*l*. EMI SE of the copper plated fabric arrived at 40-50 dB at the frequency of 6 GHz to 18 GHz when the concentration of copper sulfate was 11 g/*l*.

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