A Method of Electroless Silver Plating on the Surface of PA6 Fiber

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Abstract. A layer of silver was deposited on the surface of PA6 fiber fabric by electroless plating method to prepare silver/PA6 conductive fabric. The surface morphology and structure of the coating were analyzed by SEM and EDS. Electroless plating process conditions: 11 g/L silver nitrate, ammonia and sodium hydroxide appropriate preparation into 1.1% silver ammonia solution. Ingredients of reducing agent: glucose 10 g/L, tartaric acid 2 g/L, ethanol 100 ml/L, pH 11-13 was adjusted by adding 10 g/L sodium hydroxide solution, temperature 20-30 ℃, reaction time 3min. The resistance of the preparation of silver/PA6 fabric is less than 1 Ω/cm, elemental silver content is 100%, the conductivity is excellent, and the electromagnetic radiation resistance is excellent.

1. Introduction
PA6, also known as nylon-6, is chemically known as polyamide fiber-6. Nylon is the world's first fiber synthesized by the distinguished American scientist Carothers and his research group in 1938. This synthetic fiber, also known as “nylon”, was the prelude of China’s synthetic fiber industry. As high performance processing for the miniaturization of automotive, electrical and electronic equipment, glass fiber [1], carbon nanotube [2], fire retardant [3-6], tyre fabrics [7], mechanical equipment lightweight process faster, higher and higher demand for nylon, nylon as structural material, in particular, has toughness, heat resistance, wear resistance, chemical resistance, low friction coefficient, self-lubricating, flame retardant, the advantages of wide temperature range, easy to machining, is widely used in an industrial engineering plastic, can be used instead of the non-ferrous metal copper production machinery, chemical industry, electrical components, such as diesel engine fuel pump, water pump, high pressure sealing ring, pipeline, etc. Polyamide fiber has many advantages, but as an organic polymer, its electrical conductivity is poor, which limits its application in electronics, electricity, military and other fields, how to improve the electrical conductivity of polyamide material, is our research topic. Silver is a kind of nonferrous metal with excellent electrical conductivity, which is often used as a chemical coating on nonmetallic surface [8]. In this paper, the surface of PA6 fiber was coated with a bright silver layer by electroless plating, and the surface structure and morphology of the coating before and after electroless silver plating were characterized.

2. Experiment
Material:PA6 fabric; The chemical reagents: silver nitrate, glucose, tartaric acid, sodium carbonate, concentrated ammonia, anhydrous ethanol, sodium hydroxide, 65% nitric acid, stannous chloride, 3, 4-dihydroxyphenylethylamine, trimethylolamine, etc.
2.1. Experimental Apparatus
Scanning electron microscope (HiTACHI, su-70), energy spectrum (OXFORD), multimeter (FLUKE), electronic balance (accuracy 0.01 g), ultrasonic cleaner, magnetic stirrer, 3M tape, other conventional laboratory instruments are omitted.

Huawei honor mobile phone, China telecom mobile network (2G signal test).

2.2. Preparation of Electroless Silver-Plated PA6 Fabrics
Process flow of electroless silver plating: degreasing-washing-sensitizing A, sensitizing B-washing-activation-washing-electroless silver plating-washing-drying.

2.2.1. PA6 Pretreatment. The sample of PA6 fiber is made of fabric with grease and dirt on the surface. To cut into a certain size of PA6 fiber fabric sample after electronic weighing scales, placed in a 500 ml beaker clean, add 2 g sodium carbonate, sodium hydroxide, 1 g sodium dodecyl benzene sulfonate surfactant, add 5 mL of ethanol, and then mixed with deionized water with a 200 ml solution, in ultrasonic stirring at room temperature for 5 min, sample 2-3 times with deionized water cleaning, with 10 g/L of dilute nitric acid for 1 min. In the second step, sensitized A, the PA6 fiber sample after oil removal was completely immersed in the currently prepared sensitizing solution A, wherein the composition of the sensitizing solution A was 10 g/L SnCl$_2$ and 10 g/L HNO$_3$, followed by room temperature ultrasound for 5 min. The sample was first soaked in 10 g/L NaOH for 1min, and then washed with deionized water for 2-3 times until the pH value was 7. Third step sensitization, B will be after allergy, A treatment of PA6 fibers completely immersed in A chef sensitizing liquid sample B, including the composition of sensitizing liquid B for: containing 50 ml 0.1 mol/L 3 hydroxymethyl aminomethane, diluted with deionized water to 250 ml, the silver ammonia solution quality percentage content of 0.4%. The adding amount of AgNO$_3$ changed was 2 g, 2.75 g and 4.18 g, and the subsequent sequence operation was the same, and the mass percentage content of the corresponding silver ammonia solution was 0.8%, 1.1% and 1.67%, respectively.

2.2.2. PA6 Chemical Silvering. After silver ammonia solution activation of a certain quality of PA6 fiber sample immersed in more than 50 ml in the preparation of silver ammonia solution, adding glucose concentrate 25 mL, then add 10 g/L NaOH solution 35 mL, shake at a constant speed in a clockwise beaker 2-3 min, solution by clarification is cloudy again, clarification, a layer of bright silver plating on the specimen surface layer, the shade drying at room temperature to 24 h, surface drying. Preparation of glucose reducing solution: add 10 g glucose and 2 g tartaric acid into a beaker, add deionized water to 500 mL, heat and stir until slightly boiling, keep for 10 min, cool to room temperature, add 50 mL ethanol and 0.1 mol/L sodium carbonate, stir until the solution is even.

Chemical reaction for the formation of silver ammonia [9]:

$$2\text{AgNO}_3 + 2[\text{NH}_3\cdot\text{H}_2\text{O}] \rightarrow \text{Ag}_2\text{O} + 2\text{NH}_2\text{NO}_3 + \text{H}_2\text{O}$$ (1)

$$\text{Ag}_2\text{O} + 4[\text{NH}_3\cdot\text{H}_2\text{O}] \rightarrow 2[\text{Ag(NH}_3)_2\text{OH}] + 3\text{H}_2\text{O}$$ (2)

$$\text{Ag(NH}_3)_2\text{OH} + \text{NH}_2\text{NO}_3 \rightarrow \text{Ag(NH}_3)_2\text{N}_3\text{O} + \text{NH}_3\cdot\text{H}_2\text{O}$$ (3)

It was found that the unstable factors of the plating solution in the electroless plating process of PA6 fiber mainly came from the sharp drop of the pH value of the plating solution caused by the increase of H$^+$ concentration in the initial solution. Therefore, it was necessary to adjust the pH value
of the plating solution in the initial electroless plating process to keep the plating solution stable. In this experiment, sufficient dilute NaOH was added once before plating to maintain the PH of the plating solution between 11 and 13 during the whole plating process, thus avoiding the discontinuity of the reaction process and uneven coating caused by repeated addition of alkali. Shaking the container with uniform force instead of mechanical stirring or ultrasonic stirring, not only to avoid physical collision and lead to the plating process of peeling off, but also to ensure that the local pH too high reaction, resulting in the decomposition of the bath.

\[ 2[Ag(NH_3)_2N0_3] + C_6H_{12}0_6 \rightarrow 2Ag + C_5H_11O_5COONH_4 + 2NH_3N0_3 + NH_3 \] (4)

2.3. Performance Test
Method of test for adhesion of coatings: peel test: attach the adhesive surface of 3 M tape to a covering area of at least 30 mm², and carefully roll a fixed weight drum over it to remove all air bubbles. The adhesive strength value of the fiber tape is approximately 8 N per 25 mm width. After 10 s, strip off the tape with a steady pull perpendicular to the surface of the covering layer. If the covering layer has no glass phenomenon, it shows that the adhesion strength is good. Electric conductivity adopts bipolar resistance method: the positive and negative electrodes of the Fluke multimeter are gently in contact with the surface of the coating, keep the distance between the electrodes about 1cm, turn on the power switch and adjust to the resistance measurement file. When the resistance value is stable, the reading will be the resistance value of the coating. Electromagnetic shielding performance detection: find a place with strong indoor network signal, wrap the signal receiver end of mobile phone shell with silver coated PA6 fiber, observe the change of 2G signal of mobile phone after 1 min, and judge the shielding performance of the material by signal attenuation.

3. Results and Discussion
3.1. Coating Surface Condition
The microscopic appearance of PA6 fiber surface coating in scanning electron microscope under different concentration of silver ammonia solution is shown in figure 1.

![Figure 1. Electron micrograph of silver plating layer under different concentration of silver ammonia solution (50X): (a) 0.4% silver ammonia solution; (b) 1.67% silver ammonia solution; (c) 0.8% silver ammonia solution; (d) 1.1% silver ammonia solution.](image)

3.2. Chemical Composition and Resistance of the Coating
After X-ray photoelectron spectrometer detection, under different concentrations of silver ammonia solution, silver content in coating and effect of resistance are shown in table 1.

As can be seen from table 1, when the mass percentage of silver nitrate in ammonia solution increased from 0.4% to 1.1%, the mass fraction of metal silver reduced from PA6 fiber surface coating increased from 56.22% to 100%, and the coating thickness increased. However, the content of silver nitrate continued to increase to 1.67%, and the content of silver in the surface coating of PA6 fiber decreased to 80.72%. The coating resistance of PA6 fiber surface was detected by multimeter under different concentration of silver ammonia solution, and the specific results were shown in table 1. Under the condition of low concentration of silver ammonia solution, the silver white coating is thin
and uneven, which results in a wide range of resistance fluctuation. When the concentration of silver ammonia solution increased from 0.4% to 0.8%, silver plating was noticeably thick, uniform distribution, resistance decreased significantly, for 1-2 Ω.cm⁻¹; Silver ammonia solution concentration increase to 1.1%, the coating thicker, darker color, more uniform distribution, continue to lower resistance value, can achieve within 1 Ω.cm⁻¹; Continue to improve the concentration of the silver ammonia solution to 1.67%, dark yellow coating thicker, the distribution is uniform, resistance rose slightly, for 1-2 Ω.cm⁻¹. Above, results show that the resistance of the coating and silver ammonia solution concentration is not a linear relationship, silver ammonia concentration was 1.1% for the best conditions, more than the threshold resistance coating not up, perhaps because silver ammonia solution concentration of more than 1.1%, obviously increase the coating thickness and adhesion decreased significantly but the outermost layer of silver, lead to some loss or deposit, deposit the actual content is lower than the theoretical value of the bank of China, resistance increased.

| Testing program | The mass percentage of silver nitrate in silver ammonia solution (%) | Concentration of silver in energy spectrum (%) | Concentration of oxygen in energy spectrum (%) | Resistance (Ω.cm⁻¹) |
|-----------------|-------------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------|
| Equation (1)    | 0.4                                              | 56.22                                       | 43.78                                       | 50~70               |
| Equation (2)    | 1.67                                             | 80.72                                       | 19.28                                       | 1~2                 |
| Equation (3)    | 0.8                                              | 84.73                                       | 15.27                                       | 1~2                 |
| Equation (4)    | 1.1                                              | 100                                          | 0                                           | 0.5~0.7             |

3.3. Coating Adhesion
3,4-dihydroxy phenylethylamine surface with good adhesion properties of medium, it can be adsorbed on the surface of the medium, to improve structure on the surface of the medium, such as 3,4-dihydroxy phenylethylamine carbonyl functional groups of the hydroxyl groups can and polyamide, the hydrogen bonds formed between the interaction force between the molecules and amino good complexing with silver ion sex improves the silver plating in PA6 fiber surface deposition ability, substrate surface chemical changes in the structure of lead to the enhancement of coating adhesion. The adhesion of PA6 fibers treated with tris-HNO₃ containing organic 3,4-dihydroxyphenylethylamine and the electroless silver plating layer of PA6 fibers not treated with this solution was tested. The peeling of the silver plating layer was examined by 3M tape method, and the results were shown in table 2.

| Testing program                                      | Adhesive force |
|------------------------------------------------------|----------------|
| 3, 4-dihydroxyphenylethylamine surface treatment    | Not loose      |
| No 3, 4-dihydroxyphenylethylamine surface treatment | loose          |

3.4. Tromagnetic Shielding Properties of Pa6 Fiber Coating
The test conditions were ambient temperature 25 °C, ambient relative humidity 40-50%, and atmospheric pressure 86-106 kPa. The samples were kept in the above environment for 48 h before the test. The environmental electromagnetic noise should not affect the measurement results, as shown in table 3.

The silver-plated PA6 material can be widely used on the chassis, shell, parts or panel of electronic instruments and equipment, so as to avoid the electromagnetic radiation to the surrounding instruments and personnel, protect human health, and ensure the normal operation of instruments and equipment.
Table 3. Shielding performance of several materials to 2G signal.

| Sample                              | 2G signal attenuation of mobile phone (%)* |
|-------------------------------------|------------------------------------------|
| PA6 fabric                          | 0                                        |
| PA6 silver-plated fabric (equation (1)) | 50%                                     |
| PA6 silver-plated fabric (equation (4)) | 50%                                     |
| Aluminum foil                       | 50%                                     |

Note*: When the 2G network signal is strong, the full grid is 4, and the attenuation is 0. When the attenuation is 3 grids, the attenuation is 25%. When the attenuation is 2 grids, the attenuation is 50%. When the attenuation is 1 lattice, the attenuation amount is 75%. When the attenuation is 0 lattice, the attenuation is 100%.

4. Material Consumption

4.1. Bath Consumption

Taking 1.1% silver ammonia solution as an example, the plating solution volume and silver deposition rate of two PA6 fiber samples of 1.78 g and 2.75 g during electroless plating were investigated, and the results were shown in table 4.

Table 4. Different mass PA6 fiber bath consumption and silver loading rate.

| Sample | Before quality | After quality | Rate of silver | Bath consumption |
|--------|----------------|---------------|----------------|------------------|
| Sample 1 1.78 g | 1.98 g | 11.2% | 50 ml 1.1% silver ammonia solution; 25 ml 1% glucose reducing solution (containing 1% glucose, 0.2% tartaric acid, 10% ethanol and 1% sodium carbonate); 38 ml 1% sodium hydroxide solution. |
| Sample 2 2.75 g | 3.46 g | 25.8% | 90 ml 1.1% silver ammonia solution; 45 ml 1% glucose reducing solution (containing 1% glucose, 0.2% tartaric acid, 10% ethanol and 1% sodium carbonate); 68 ml 1% sodium hydroxide solution. |

4.2. Sensitizing Fluid Consumption

The sensitization was divided into two steps: A and B, in which A was the sensitization of stannous chloride and B was the sensitization of tris-HNO₃ of 3, 4-dihydroxyphenylethylamine. Due to the oxidation of tin ion is easy to tetravalent tin ion, tetravalent tin ion is easy to hydrolyze and produce colloidal precipitation so that the sensitization solution failure, so should be ready to use, try to use within 24 hours. In step B, the stability of 3, 4-dihydroxyphenylethylamine is poor, especially in strong alkaline conditions, it is easy to occur intermolecular polymerization, while trimethylolamine is a strong base, acid should be added to adjust the PH value of solution 2-7, in order to make 3, 4-dihydroxyphenylethylamine stable existence, the replacement cycle of sensitizing solution B is 7-15 days. The consumption of sensitizing fluid is shown in table 5.

Table 5. Composition and consumption of sensitized solution.

| Category and content | Sensitizing solution | Sensitizing liquid B |
|----------------------|----------------------|----------------------|
| Composition          | 200ml 1% stannous chloride solution (containing stannous chloride 1%, 65% nitric acid 2%) | 200ml 0.6% solution (containing Tris base 0.6%, 65% nitric acid 0.5%, 3, 4-dihydroxyphenylethylamine 0.5‰) |
4.3. Consumption of Oil Remover

PA6 fiber surface tension decreased significantly after oil removal, easy to order after sensitization, in addition to the agent is composed of inorganic alkali and anionic surfactant, sodium hydroxide, sodium carbonate 1 g, 2 g into them 1 g sodium dodecyl benzene sulfonate surfactant, add 5 ml of ethanol, and then mixed with deionized water with a 200 ml solution, in ultrasonic stirring at room temperature for 5min. The replacement cycle of oil remover is 15 to 30 days.

5. Conclusion
(1) It is feasible to prepare PA6 polyamide fiber by electroless plating.
(2) PA6 was sensitized with bivalent tin ion, then soaked with tris-HNO$_3$ buffer containing 3, 4-dihydroxyphenylethylamine, and then electroless plating was carried out to obtain solid silver coating.
(3) Examines the quality score were 0.4%, 0.8%, 1.1%, 1.67% of silver ammonia solution on the influence of coating resistance, when silver ammonia solution quality percentage is 1.1%, PA6 fiber coating resistance value of the lowest, 0.5-0.7 $\Omega$.cm$^{-1}$; When silver ammonia solution quality percentage is 0.4%, PA6 fiber coating has the highest resistance, 50-70 $\Omega$.cm$^{-1}$.
(4) Silver-coated PA6 has significant electromagnetic shielding effect on 2G signal.

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