Electrochemical Deposition of Copper on Polymer Fibers

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ABSTRACT

In this study, we report the fabrication of functional complex fibers, which have been studied widely globally for numerous applications. Here, we fabricated conductive complex fibers with antibacterial properties by coating metal ions on the surface of plastic (polypropylene) fibers using the electroless and electrochemical deposition. First, we polished the polypropylene melt-blown fiber surface and obtained an absorbing Pd seed layer on its surface. Subsequently, we substituted the Pd with Cu. Bis-3-sulfopropyl-disulfide disodium salt (SPS), polyethylene glycol (PEG), and ethylene thiourea (ETU) were used as the brightener, carrier, and leveler, respectively for the electroplating. We focused on most achieving the stable plating condition to remove dendrites, which are normally during electroplating metals so that smooth layer is formed on the fiber surface. The higher the amount of SPS, the higher was the extent of irregular plate-like growth. Many irregularities in the form of round spheres were observed with increase in the amount of PEG and ETU. Hence, when the additives were used separately, a uniform coating could not be obtained. A stable coating was obtained when the three additives were combined and a uniform 5-9 μm thick copper layer with a stable morphology could be obtained around the fiber. We believe that our results can be applied widely to obtain conductive fibers with antibacterial properties and are useful in aiding research on conductive lightweight composite fibers for application in information technology and robotics.

Keywords : Electroless plating, Electrochemical plating, brightener, Carrier, Leveler

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1. Introduction

The fiber industry, which is one of the oldest industries in the human history, has undergone various changes so far and functional and industrial fibers are expected to dominate the field in future. The fiber industry of the 21st century is predicted to experience a high growth rate of > 6 % per annum by 2025 because of the development of functional and industrial fibers, which will find wide applications in environmental and information technology-related sectors. The competition within the fiber industry is expected to increase because of international labor division and trade liberalization. Developing nations are expected to make rapid progress in the traditional fiber industry sector because of the abolition of the

fiber quota system, and the importance of China is expected to rapidly grow, with its membership in the World Trade Organization. On the other hand, for industrial and functional fiber sectors, which are considered high value added and high-tech businesses, the investment on research and development and technology competition has become stupendously increased among advanced countries such as Korea.

With changes in the trends of the world fiber market, future fiber industry products, and fiber technology, Korea has already begun to develop functional fibers in earnest, spurred by interest from the government. Various types of functional fibers were developed for application in nanotechnologies, various digital and smart industries, artificial intelligence, and biomedical engineering. For biomedical applications, the demand for antibacterial products, which purify air and liquid, has increased drastically because of an increased interest in environment and hygiene. The

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world market size of antibacterial products reached 3.4 billion US dollars in 2000 and is rapidly growing over 15 % every year. The market size in Korea, which was about 350 billion KRW in 2000, shows a more rapid growth than the world market. The air filter market can be divided into products used for in-house use, such as air conditioners and air cleaners, and those for industries, such as industrial heating, ventilating, and air conditioning filters, and air conditioning products used in automobiles. The demand of air cleaners shows a steady growth despite the slower sales of home appliances during economic depression [1]. In addition, due to the increased demand for products enhancing a healthy life, the domestic market size of water purifiers has increased to 1 trillion KRW and many home appliance producers are investing in the water purifier market as a new business with market shares of 60 % for simple water purifier, 30 % for mineralized water purifier, and 10 % for processing some specially functionalized water. The trend shows an increase of market for pure water bestowing health benefits and the potential of functionalized water market is much larger than the other industries.

In this study, we have used electroless plating without organic and inorganic binders to obtain antibacterial non-woven fabrics for water filter applications, exhibiting stronger antibacterial activity than existing antibacterial non-woven fabrics. Deposition of metallic ions on fiber surfaces using the electroless plating method has been widely studied. For effective plating, various methods, such as the use of ethylenediaminetetraacetic acid, formaldehyde, and organic additives [2-4] and injecting of various reducing agents, such as hydrazine, sodium hydride, sodium citrate, and diethylamineborane into the plating solution have been used [5-8]. There are many studies focusing on replacing the conventionally used, but expensive, Pd [9]. However, in this research, Pd plating was used to achieve a basic adhesive strength by creating a seed layer on the clean fiber at the first stage of plating [10-13]. Subsequently, various organic additives were added to the seeded layer to control deposition of metal from metal ions to obtain a layer with the required fine structure [14,15].

2. Experimental Section

2.1 Electroless plating of Cu

Plating baths were equipped with a heater and con-

troller and separate baths were used for each process because the differences in the chemicals and temperature required for each process. Spunbonded polypropylene non-woven fabric (60 g/m², Toray) and Spunbonded polyester nonwoven fabric (60 g/m², Dongyang), the most common fibers in the fabric industry, were used as the test samples. Samples were soaked in NaOH at 70 °C for 3 min for degreasing. Then, the samples were soaked in another bath with KMnO₄ and H₂SO₄ for 5 min at 70 °C to polish the surface to achieve an anchoring effect. Then, the samples were cleaned with H₂C₂O₄ to remove the acid radicals and dipped in a PdCl₂-HCl solution for 5 min to activate Pd substitution of the already formed Sn layer [16]. Then, electroless Cu plating was carried out for 20 min in a bath containing CuSO₄, NaH₂PO₂, NiSO₄, and Na₃C₆H₅O₇ at an appropriate concentration (as shown in Table 1) [17,18]. The reduction potential of each element is shown below.

The surface of the fiber and plated copper particles were analyzed using SEM (scanning electron microscopy) and EDX (energy dispersive X-ray spectroscopy) to obtain the morphology and composition of the electrodeposited particles, respectively.

2.2 Electrodeposition

Electroplating was carried out by including bis-3-sulfopropyl-disulfide disodium salt (SPS), polyethylene glycol (PEG), and ethylene thiourea (ETU) as the brightener, carrier, and leveler, respectively to the aqueous copper sulfate solution with 50 ppm Cl⁻. The additives were used to control the growth rate of copper during deposition [14,20,21]. A rectifier was used as the plating equipment and Pt anode and biodegradable polypropylene nonwoven fabric with electroless plated copper cathode were used. The experiment was carried out at room temperature in a glass beaker, which served as the electrolyte bath.

After deposition, the test samples (1 cm wide and 4.5 cm tall) were dipped into 100 g/L of aqueous sul-

furic acid for 2 s. Then, the samples were rinsed with water for 30 s to remove foreign substances. To the best of our knowledge, not many studies focus on electroplating common fibers for filter applications. Therefore, we have changed the plating solution to match the conventional concentration used and we have used additives known to modulate the electrodeposition speed and other characteristics. The bath conditions used here are provided in Table 2. A low current density was used because plating within the fiber does not occur at high current densities because of an increase in the throwing power. When the plating leads to an excessively thick coating, the flow rate sharply decreases because the distance between the fibers decreases. Accordingly, the plating time was adjusted to obtain thin coatings with a thickness of 20–25 μm . To minimize the number of variables, the copper and sulfuric acid concentrations were fixed. SPS is known to increase the plating speed and PEG enables electrodeposition in the deeper portions of the objects by preventing leaning and flowing of current. Table 1 shows the correlation between the electrodeposition conditions such that the most optimal plating can be achieved [20]. The theoretical amount of electrodeposition is calculated by limiting the area of the cathode. We confirmed that the fiber was well deposited overall, and the amount of electrodeposition was also determined using SEM. SEM was also used to characterize the fiber surface and the plated particles, while the composition of the electrodeposited particles was analyzed by EDX. The antibacterial activity of the obtained fiber was determined using *Staphylococcus Aureus* ATCC and 6538 *Staphylococcus Aureus* ATCC 6538.

3. Results and Discussion

3.1 Effect of plating time on the morphology of the electroless plated layer

Metals can be deposited on a non-conductive fiber

surface regardless of the fiber type after degreasing and etching (Fig. 1) [19]. The bath conditions shown in Table 1 are the conditions used for the electroless plating of polyesters like polyethylene terephthalate, which is the most widely used industrial plastic fiber, and spunbonded polypropylene. While it is known that the amount of material electrodeposited increases with time, the SEM-EDX analysis reveals hardly any change in the morphology and composition. Hence, changing the electrodeposition time leads to changes in the amount of materials deposited, while the composition remains unaffected. However, increasing the thickness by increasing the plating time is not required during electroless plating because the thickness and the antibacterial activity can be increased during the subsequent electroplating step. In addition, if an excessively long time is used for obtaining the seed layer, loss of uniformity is observed, which may lead to the growth of unnecessary structures, which in turn lead to removal of plated layers, affecting the subsequent electroplating step. Hence, it is advisable to keep the electroless plating time short to obtain the minimum amount of seeds required.

Fig. 1. Scanning electron microscopic (SEM) images of electroless plating of Cu on the surface of (a, b) polyester and (c, d) polypropylene.

Table 1. Bath and operating conditions of electroless plating.

Bath conditions	Reagents	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	NaH_2PO_2	NiSO	H_3BO_3	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$
	Concentration (g/L)	8	30	1	30	15
Operating conditions	pH	4	9		10	11
	Temperature ($^{\circ}\text{C}$)	70	70		70	70
	Time (min)	20	20		20	20

3.2 Effect of pH on the morphology of electroless plated samples

The composition and structure of the plated layers

Fig. 2. SEM images of electroless plated samples obtained at different pH of (a) 4, (b) 9, (c) 10 and (d) 11.

Fig. 3. Elemental analysis estimated from energy-dispersive X-ray (EDX) spectroscopy of samples obtained by electroless plating at different pH.

are dependent on the pH change during electroless plating partly because of the variation of the concentration of the major metallic component in the electrolyte [3,17]. As shown in Fig. 2 and 3, the EDX analysis shows that the copper content in the plated sample is highest when the plating solution pH is 10. Hence, the optimal condition for copper plating can be identified.

3.3 Effect of additives

In general, the brightener, carrier, and leveler are used as electroplating additives [14]. In the present study, we used a plating solution with conventionally used copper sulfate and sulfuric acid [14,15] and the concentration of the additives was fixed at 5-20 ppm (Table 2) [20]. We compared the morphology of copper deposited on fibers when the additives were used separately and when none of the additives were used. Without additives, the copper deposited was irregular and unstable and a similar structure was obtained when only the brightener was added. The copper was deposited in acicular shapes when the leveler and carrier were added. Hence, when the additives were used individually, unstable and non-uniform products, as shown in Fig. 4, were obtained. While the brightener agglomerates particles to form larger clusters, the leveler and carrier break the copper particles into smaller pieces.

3.4 Effect of the brightener

The brightener was added separately to the bath to obtain find the optimal brightener concentration during electrodeposition. As shown in Fig. 4, unstable electrodeposition and structures resembling spilt keratins were obtained when the SPS concentration was 1, 5, or 10 ppm. The number of overgrown nodules increased at 20 ppm and stable and evenly plated layers were obtained at 15 ppm.

Table 2. Bath and operating conditions of electroplating with different concentration of additives.

Bath conditions	Reagents	CuSO ₄ ·5H ₂ O			H ₂ SO ₄		Cl ⁻
	Concentration	100 g/L			100 g/L		50 ppm
Additives	Brightner (ppm)	7	15	30	7	15	30
	Carrier (ppm)	12, 18, 36 and 54			12, 18, 36 and 54		
	Leveler (ppm)	12			18		
	Temperature (°C)	25			25		
Operating conditions	Time (min)	30			45		
	Current density (A/dm ³)	6			6		

3.5 Effect of the carrier : leveler ratio

The experiment was carried out with the conventionally used brightener: (leveler + carrier) ratio of 1:2. As noted previously, 15 ppm of brightener leads to stable electrodeposition; however, the amount of carrier + leveler should be maintained at 30 ppm, while changing the ratio of the two additives (Fig. 4). A ratio of 3: 2 (Fig. 4d) leads to the most stable surface, while other ratios lead to keratin-like shapes or fine cracks on the surface. The optimum ratio (3:2) of the two additives was advantageous to deposit Cu on the front fibers uniformly and effectively, resulting in smooth and homogeneous Cu-coated surface, however, the deposition of Cu on the rear or deeper fibers was irregular and non-uniform due to the drop of chemical potential in the fibers at the deeper level.

3.6 Effect of plating time and composition of additives on the morphology

Changes in the structure of the deposited surface were observed by changing the concentration of each additive by 10 %. Further, the structural changes with variation of plating times were analyzed simultaneously. The surface magnified to 500 times became irregular and showed unstable growth when the leveler and carrier were used in excess, while the deposition was stable when the brightener concentration was low. We confirmed that the surface that appeared stable when magnified to 500 times was irregular and

unstable when magnified to 5000 times (Fig. 5). The overall surface morphology did not change significantly when the thickness increased with increase in plating time.

3.7 Optimization of additives

To identify the effect of plating conditions, the morphology of the copper layer deposited on the fiber was analyzed for various electrochemical Cu plating conditions without any additives and with different concentrations of the brightener, leveler, and carrier. When the leveler and carrier were used together, the structure of the deposited copper changed to an acicular form. Hence, the brightener leads to agglomeration of the particles, while the leveler and carrier breaks copper particles into smaller pieces. The brightener concentration required to achieve the most stable electrodeposition was obtained by modulating the relative ratio in the initial values used. The most stable deposit was achieved when the concentration was < 10 ppm. When the concentration exceeded 30 ppm, bumpy structures were obtained on the fiber and irregular growth with fine structures was observed. In addition, the leveler-carrier ratio required to achieve the most stable electrodeposition was also optimized to reduce irregular growth, defects, and fine structure. The most stable electrodeposition was achieved when the amount was raised to 200 % (Fig. 6).

Fig. 4. SEM images of (a) polypropylene (PP) fibers, (b) PP fibers after electroplating of Cu without additives, (c) PP fibers after electroplating of Cu using only the brightener at 15 ppm, and (d) PP fibers after electroplating of Cu using carrier:leveler ratio at 12 ppm:18 ppm (3:2, v/v).

Fig. 5. Changes in the SEM morphologies as a function of the plating time and additives concentration (a) SPS 16.5 ppm, PEG 18 ppm, ETU 12 ppm, (b) SPS 15 ppm, PEG 20 ppm, ETU 14 ppm and deposition time = 30 min, (c and d) the samples were obtained under the same conditions with deposition time of 45 min.

Fig. 6. SEM morphologies after changing the concentrations of brighteners at (a) 5 ppm, b) 15 ppm, and total concentration of the carrier + leveler (3:2, v/v), (c) 30 ppm and (d) 60 ppm.

Fig. 7. SEM Morphologies changing as a function of the additive concentrations (a) 50 % decrease in comparison to the conventional ratio, (b) conventional ratio (SPS 15 ppm, PEG 18 ppm, and ETU 12 ppm), (c) 200 % total increase, and (d) brighter 200 %, leveler + carrier 210 %.

3.8 Optimization of the ratio of additives

Fine structure was less fine and much defects were found when the amount of additives was lower than the conventional values used. When the amount of brightener was further increased by 10 % after increasing the amount of brightener by up to 200 %, the fine structure was unstable. In contrast, when the amount of leveler and carrier was increased to more than 210 % to 300 %, stable plating was achieved (Fig. 7). The plated layer thickness varies with plating time and in this study, a deposition thickness of about 27 μm is achieved on a flat layer. Under the

Fig. 8. SEM images of the section morphology after electroless plating and electroplating. (a) Cross-section of electroless plated fiber (thickness 1.6 μm) and (b) the cross-sectional image of the electroplated fiber (thickness 4.6–6.6 μm).

same conditions, a 4–6.5 μm thick copper layer is deposited on the surface of a round fiber. The difference is because the fiber surface is not flat and copper particles penetrate into non-woven fiber and layer obtained after each deposition is thin. The difference in fibers can also be attributed to the gap of strength, which receives current (Fig. 8).

4. Conclusions

This research aimed to deposit stable structured copper layers on polypropylene spun yarn non-woven fabric fiber by electroless deposition to seed copper and by a subsequent electroplating step. In electroless plating, the copper structure and composition varied with the pH of the plating solution. The morphology and composition of the electrodeposited copper were characterized by SEM and EDX and the optimum plating conditions were identified. The additives, including a brightener, leveler, and carrier were used for the electrodeposition. The specific roles of these additives were identified by analyzing the structure and morphology of the electrodeposition. A low current density of 6 A/dm^2 was used because the

deposits are required to penetrate into the fiber, while maintaining plating on the outerlayers. The observed results indicate that stable plating cannot be achieved when the three additives were used individually and the conventionally used composition of these additives is not applicable to plastic fibers. Leveling is achieved when the leveler and carrier concentrations (in comparison to conventional concentrations) were increased to > 200 %. Electroless plating led to a copper layer with a thickness of 1.5 μm and electroplating resulted in a stable plated layer, 4-6.5 μm in thickness. We predict that a denser copper layer can be formed from electroplating with a bath using lesser concentration of additives if a denser and more uniform seed layer can be obtained by changing the temperature during electroless plating or by altering the Ni concentration in the plating bath [3,17]. In terms of the brightener, the monosulfide series of additives is known to increase the flexibility by changing the structure of plated layers. It is expected that we can achieve improved results if more appropriate concentration and plating conditions can be used in the two steps.

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