Metallization of Textile by Pt Catalyzation in Supercritical Carbon Dioxide and Pt Electroless Plating for Applications in Wearable Devise

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Abstract

In this study, an electroless plating method involved Pt catalyzation in supercritical carbon dioxide (sc-CO₂) and conventional Pt electroless plating was used for the metallization of polyamide 6,6 (PA66) textiles. The catalyzation was conducted either by conventional method at atmospheric pressure or in sc-CO₂ with bis (2,4-pentandionato)-platinum. After the catalyzation process, the conventional Pt electroless plating method was performed for the Pt catalyzed PA66 textiles. Surface of the Pt coated PA66 was observed by an optical microscope and a scanning electron microscope. The Pt coating by the conventional catalyzation had a rough surface, and the surface did not show the textile outline because of the dissolution of the textile in the conventional catalyzation solution. The textile metallized by the sc-CO₂ catalyzation showed a metallic bright coating, and the Pt coating was observed on the surface of each fibers. These results indicate that the sc-CO₂ catalyzation is a promising method to catalyze the PA66 textile.

Keywords: metallization, textile, polyamide, platinum, supercritical carbon dioxide

1. Introduction

Wearable device is an advanced technology that involves metallization of textiles for applications in various fields [1-3]. One of the challenging points in fabrication of the wearable device is the deposition of metallic materials on the textile. There are many methods that could be applied to deposit metallic materials on the textile, such as sputtering [4], chemical vapor deposition [5], laser-assisted metallization [6] and electrostatic spray deposition [7]. Among the metallization methods, electroless plating is the most promising method in the industrial level because of its simple operation and low cost process. Therefore, studies on fabrication of the fiber coated with metallic materials by electroless deposition have attracted much attention. However, there are still some points needed to be improved in the conventional electroless plating method. First, a pretreatment process is usually needed to improve adherence of the metallic coatings on the fibers, and toxic chemicals are often used in this step. In this case, residual of the toxic substances raises concerns for practical use of the fibers in clothing. Second, the fibers can be damaged or even lost because of the strong acid used in the pretreatment.

Supercritical carbon dioxide (sc-CO₂) is non-polar and has physical properties between those of gas and liquid. Most importantly, CO₂ is non-toxic and abundant in

the environment. Hence, sc-CO₂ is used as non-toxic solvents in extractions, separations, chemical reactions, and various other applications [8]. Recently, several studies on the deposition using sc-CO₂ have been reported, such as a supercritical fluid deposition [9-13] and copper electroplating with sc-CO₂ using organo copper complex as the source of copper [12]. Sc-CO₂ is reported to be able to penetrate into the structure of polymers because of the non-polar and zero surface tension properties. Based on this, metallization of polymeric substrate by electroless plating utilizing sc-CO₂ has been demonstrated [13]. The sc-CO₂ is used in the catalyzation step with an organo Pd complex as the source of the Pd catalyst, and coverage and adhesion of the metal coatings on the polymer substrate, such as Kapton® polyimide film, are reported to be improved. Therefore, we suggest the sc-CO₂ catalyzation (SCC) can also be applied in metallization of polyamide 6,6 (PA66) textile to solve the problems of the toxic chemicals used in the pretreatment and to improve adhesion of the metal coating on the textile. PA66 is also known as nylon 6,6, which is extensively used in the fiber industry and various other fields because of the high crystalline melting point, good resistance to hydrocarbons, high strength, high biocompatibility, and simple fabrication process [14]. Thus, PA66 textile is selected as the substrate material in this study,

The biocompatibility is the most important factor for the applications in wearable

1 devices. Therefore, Pt was chosen as the catalyst in the electroless plating and the metal
2 deposited on the textile in this study. This is because, Pt has better biocompatibility than
3 Pd often used in the conventional catalyzation [15].

4 In this paper, metallization of the PA66 textiles with an improved biocompatibility by
5 having Pt as the catalyst and the metallic coating on the PA66 textile is reported. Also,
6 the SCC would be applied to eliminate the toxic chemicals often used in the
7 catalyzation step and improve the quality of the Pt coatings on the PA66 textile. The
8 PA66 metallization method proposed in this study is promising for applications of the
9 metallized fibers in the wearable devices because the concerns from the residual toxic
10 substances and the possible metal allergy symptom caused by Pd and Ni could all be
11 eliminated.

12 13 **2. Experimental**

14 **2.1. Experimental apparatus**

15 The high pressure apparatus (Japan Spectra Company) used in this investigation is
16 shown in Fig. 1. The reaction chamber was made of stainless steel 316 vessel with an
17 inner volume of 50 ml. The reaction chamber was placed in a temperature-controlled air
18 bath to control the experimental temperature. The PA66 textile was positioned in the
19 reaction chamber using a plastic-coated platinum wire.

2.2. Materials and sample preparation

In this study, CO₂ having purity of 99.99 % was used. A PdCl₂/SnCl₂ solution consisted of PdCl₂ (100 mg/l), SnCl₂ (10 mg/l) and HCl (87.5 g/l) was used for the conventional catalyzation (Conv-Cat). Bis (2,4-pentandionato)-platinum was used as the source of Pt in the SCC. The Pt plating bath was commercially available electrolyte purchased from MATEX Japan, and it was consisted of MATEX PLATINUM basic bath (500 ml/ 1L), MATEX PLATINUM reduction agent (10 ml/ 1 L), NH₃ solution (50 ml/ 1L), and ion-exchanged water (460 ml/ 1L). Platinum concentration in the plating bath was 2 g/L. The pH of this bath was 12. The textile used in this study was made from PA66 fibers. Image of the untreated PA66 is shown in Fig. 2(a).

2.3. Catalyzation process

No pretreatment was conducted in this study. Two types of catalyzation procedures were performed. The temperature used in the Conv-Cat was room temperature. The time used in the Conv-Cat was 10 s. The temperature of the SCC was 353 K, and the pressure for the SCC was 15 MPa. The time of the SCC was 2 h.

2.4. Electroless deposition

After the catalyzation process, the conventional electroless plating (Conv-EP) was performed. The catalyzed textile was immersed in the Pt electroless plating bath at 333 K. Two immersion times were used, which are 3.5 and 4 h.

2.5. Analysis

Surfaces morphology of the Pt coated PA66 textiles was observed by an optical microscope (OM, KEYENCE: VHV-5000) and a scanning electron microscope (SEM, JEOL: JSM-7500).

3. Results and discussion

3.1 Surface morphology

Images of the PA66 textiles treated by the Conv-Cat and 3.5 and 4 h of the Conv-EP are shown in Fig. 2(b) and (c), respectively. By comparing appearance of the Conv-Cat and Conv-EP treated PA66 textiles with the untreated PA66 textile shown in Fig. 2(a), surface of the Conv-Cat treated PA66 fibers was rough and a few white particulates was observed under the OM. The results were suggested to be caused by the acid used in the Conv-Cat step. Rough surface is usually beneficial in metallization of polymers. However, surface of the Conv-Cat treated PA66 fibers did not show obvious appearance of any metallic coating after 3.5 h of the Conv-EP process. When the Pt plating time was increased to 4 h, the appearance was still similar to that of the 3.5 h case.

The SCC and Conv-EP treated PA66 textiles are shown in Fig. 3. After the Conv-EP for 3.5 h, shown in Fig. 3(a), surface of the PA66 fibers was found to be covered by bright Pt coating. The Pt coatings seemed to be very thin in the OM observation. Therefore, a longer plating time of 4 h was used to increase the coating

1 thickness. As shown in Fig. 3(b), much thicker Pt coating was observed on the PA66
2 fibers. Although the Pt coating became much thicker after 4 h of the plating, the outline
3 of the fibers could still be seen.

4 More details of the Pt coatings could be observed from the SEM images in Fig. 4.
5 For, the Conv-Cat and Conv-EP treated PA66 textiles, the surfaces were rough, and it
6 was difficult to identify outline of the fibers because boundary between each fibers was
7 not clear, shown in Fig. 4(a) and (b). Also, there was not much difference when the
8 Conv-EP was increased from 3.5 to 4 h. These results were in agreement with the
9 surface morphology observed by the OM and confirmed that the Conv-Cat process was
10 not appropriate for metallization of the PA66 textiles. This is because; damage of the
11 PA66 and deformation of the fibers occurred in the Conv-Cat step. The acid used in the
12 $\text{PdCl}_2/\text{SnCl}_2$ solution can react with the PA66 polymer chains. Then, subsequent
13 disruption of the hydrogen bonds between the polymer chains occurred [16].

14 In Fig. 4(c), the SEM image shows that the SCC and Conv-EP for 3.5 h could
15 produce pinhole-free and smooth Pt coatings on the PA66 fibers. Furthermore, the Pt
16 coating on the surface of each fiber still showed outline of the fibers. No peeled-off part
17 was observed. These results demonstrate that the SCC was an excellent catalyzation
18 process to improve the adherence of the metal coatings on the textile. The adherence
19 was improved by the anchoring effect, which metal roots were formed under surface of
20 the polymers to anchor the metal coatings [11,13]. The metal roots were formed by
21 impregnation of the Pt catalysts into the polymer by the sc-CO_2 . The solubility of bis
22 (2,4-pentandionato)-platinum in pure sc-CO_2 is high, and sc-CO_2 can penetrate into the
23 structures of polymers because of the non-polar and zero surface tension properties [17].

So, the catalyst could be transferred into the polymer structure to form catalyst seeds in the polymer. Then, reduction of the metal ions could be initiated at the catalyst seeds for form metal roots to anchor the metal coatings.

Fig. 4(d) shows the Pt coating by the SCC and Conv-EP of 4 h. With a longer plating time, the Pt coating thickness is expected to be higher. The result showed that the outline of the fibers was still obvious with a thicker Pt coating, but some cracks were observed. The cracks were suggested to be mostly caused by the differences in elastic constant between Pt and PA66. A longer plating time could also lead to a larger internal stress in the plated film, which can lead to the cracks or peel-offs.

4. Conclusions

In this study, Pt metallization of the PA66 textiles was realized by the sc-CO₂ catalyzation and the conventional electroless plating. When the PA66 textiles were catalyzed in the PdCl₂/SnCl₂ mixture solution, it was difficult to have complete coverage of the Pt coatings on the PA66 fibers, and the fibers were found to be damaged. The damage was suggested to be caused by the acid used in the Conv-Cat process. On the other hand, complete coverage of the PA66 textiles with defect-free bright Pt coatings was obtained when the SCC was applied. For the Pt metallization of PA66 utilizing the SCC, improved bio-compatibility by replacing Pd with Pt, exclusion of the toxic chemicals used in the catalyzation step, and Pt coatings with enhanced adherence on the PA66 are the promising points for the applications in wearable devices.

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2

3 **Figure captions**

4 Figure 1. (a) CO₂ gas tank, (b) CO₂ liquidization unit, (c) liquidization unit, (d) high
5 pressure pump, (e) thermal bath, (f) reaction-cell (PEEK-lined SUS316L), (g) substrate,
6 (h) cross stirrer, (i) back pressure regulator, and (j) trap.

7

8 Figure 2, OM images of the (a) untreated PA66 textile and PA66 textiles treated by (b)
9 Conv-Cat and Conv-EP for 3.5 h and (c) Conv-Cat and Conv-EP for 4 h.

10

11 Figure 3, OM images of the PA66 textiles treated by (a) SCC and Conv-EP for 3.5 h
12 and (b) SCC and Conv-EP for 4 h.

13

14 Figure 4, SEM images of surface of the Pt coatings by (a) Conv-Cat and Conv-EP for
15 3.5 h, (b) Conv-Cat and Conv-EP for 4 h, (c) SCC and Conv-EP for 3.5 h, (d) SCC and
16 Conv-EP for 4 h.

Figure 1. (a) CO₂ gas tank, (b) CO₂ liquidization unit, (c) liquidization unit, (d) high pressure pump, (e) thermal bath, (f) reaction-cell (PEEK-lined SUS316L), (g) substrate, (h) cross stirrer, (i) back pressure regulator, and (j) trap.

Figure 2, OM images of the (a) untreated PA66 textile and PA66 textiles treated by (b) Conv-Cat and Conv-EP for 3.5 h and (c) Conv-Cat and Conv-EP for 4 h.

Figure 3, OM images of the PA66 textiles treated by (a) SCC and Conv-EP for 3.5 h and (b) SCC and Conv-EP for 4 h.

Figure 4, SEM images of surface of the Pt coatings by (a) Conv-Cat and Conv-EP for 3.5 h, (b) Conv-Cat and Conv-EP for 4 h, (c) SCC and Conv-EP for 3.5 h, (d) SCC and Conv-EP for 4 h.

Supercritical CO₂ Catalyzation (SCC)

Organo Pt complex
are soluble in
supercritical CO₂
(sc-CO₂)

Pt coated PA66 textiels

Not coated with Pt

Uniform Pt coating