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Impregnation of Metal Complex into polymers Using Supercritical Carbon Dioxide and Their Metal Plating

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ABSTRACT

The mechanism of supercritical fluid dyeing was made clear by summarizing the swelling behavior of fiber materials in $scCO_2$, solubility of dyes into $scCO_2$ and diffusion coefficients of the dyes from $scCO_2$ fluid in the fibers [1,2]. Appling this principle the other textile processing was investigated, for example, the impregnation of functional polymers into fibers, the fixation of functional natural compounds on the textiles, the polymerization of functional monomers in the fibers and metal plating on the fibers and textiles.

1. INTRODUCTION

Water has been used as a medium in dyeing process over a millennium. The dyeing is a characteristic industrial process where a plenty of water and energy are consumed. Besides, an installation of equipments for treatments of wasted water requires high initial const.

In 1991, a great attention was given on the report describing the novel dyeing method with use of supercritical carbon dioxide ($scCO_2$) [1]. This new dyeing method has many advantages such high dyeing rate, no requirements of post-treatments and no waste treatments. Recently, the mechanism of the supercritical fluid dyeing (SCFD) was made clear by summarizing solubility behavior of the dyes, swelling of the fibers in $scCO_2$, dyeing isotherms and the other physicochemical properties of the fibers in $scCO_2$.

In this paper, the other textile processing will be introduced, applying the principle of SCFD, for example, the impregnation of functional polymers into fibers, the fixation of functional natural compounds on the textiles, the polymerization of functional monomers in the fibers and metal plating on the fibers and textiles.

2. EXPRIMENTAL

In the SCFD, the disperse dyes dissolved in $scCO_2$ were impregnated and adsorbed onto the fibers (see Fig.1). Applying this principle, the other compounds should be impregnated and fixed into fibers.

2.1 Impregnation of metal complex into fibers and metal plating

In contrast to the pretreatment technology used in the conventional electroless metal plating of polymer materials, our newly developed supercritical pretreatment technology significantly reduces the large amount of wastewater necessary for the old process. In this new pretreatment process, palladium (II)-hexafluoroacetylacetonate ($Pd(hfa)_2$) is impregnated into Kevlar® fiber/fabric, and it can be easily activated by overheating without hydrogen. The treated Kevlar® fiber/fabric immersed in the electroless copper plating solution is coated with a shining copper film

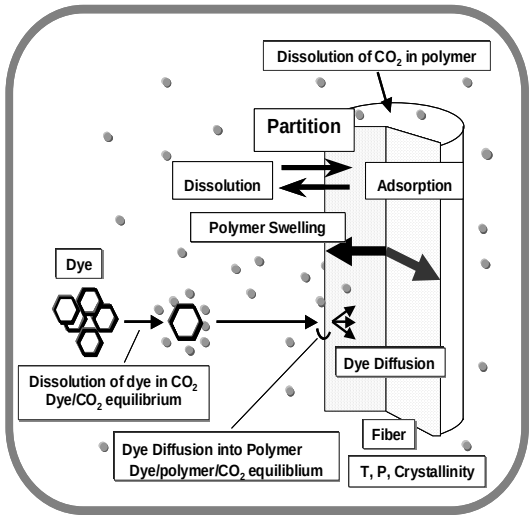

Fig.1 Mechanism of supercritical fluid dyeing (modified Schollmeyer's Model).

in a short time (Fig.2). By increasing the supercritical pretreatment time (range: 0–60 min) and the amount of $Pd(hfa)_2$, it is possible to induce more copper to adhere to the impregnated Kevlar® in the same plating period.

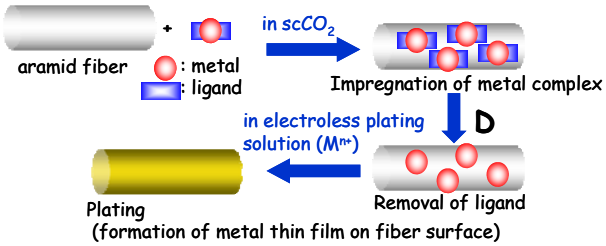

Fig.2 Process of electroless plating of aramid Fibers using $scCO_2$.

The $scCO_2$ dissolves solid compounds like liquids do while its viscosity is low and diffusibility is high like gases [3]. Due to these properties, $scCO_2$ offers the intriguing opportunity to substitute toxic organic solvents for environmentally friendly carbon dioxide to dissolve organometallic compounds and effectively impregnate them into the swelling polymer [3-8]. Consequently, a metal film is easily adhered on the polymer material surface by following treatment in electroless plating solutions. Watkins

and other researchers impregnated organic-metal complexes

Kevlar®-29 fiber (DTX: 1670, DEN: 1500), Kevlar® T732 and T740 fabrics provided by the DuPont-Toray were ultrasonically washed in acetone before experiments. A certain amount of palladium (II)hexafluoroacetylacetonate ($Pd(hfa)_2$) purchased from the Aldrich Chemical Co. and Kevlar specimen were loaded in a sample cartridge attached to a batch-type supercritical extractor (SFE System 2200, ISCO, USA). After the temperature was reached at 150 °C, carbon dioxide was added via the high-pressure syringe pump to the desired pressure. The impregnation lasted for 60 min, and then the decompressed sample was taken out within 5 min.

The thermal decomposition of the Pd complex was characterized by thermal gravimetric analysis (TGA) with TG/DTA32 (Seiko Instruments, Inc.). Fig.3 shows that $Pd(hfa)_2$ is decomposed at 90– 154 °C. Thus, the Kevlar® fiber/fabric was treated in $scCO_2$ with a certain amount of $Pd(hfa)_2$ for 5–60 min at 150 °C. The color of the samples changed from bright yellow to gray yellow.

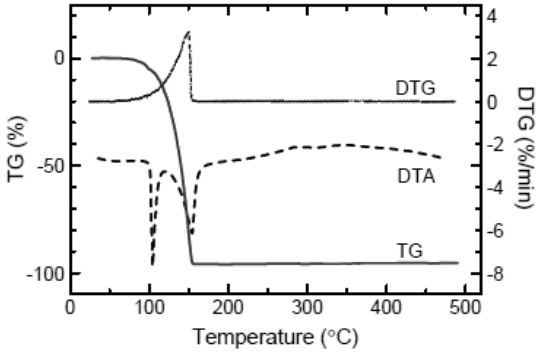

Fig.3 Combined thermogravimetric(TG), differential thermo-gravimetric (DTG), and differential thermal analytic (DTA) curves of $Pd(hfa)_2$ in a dynamic argon atmosphere.

The Kevlar® samples impregnated with $Pd(hfa)_2$ in $scCO_2$ at 150 °C and 15 MPa for 15 min. were analyzed by X-ray photoelectron spectroscopy (XPS) to identify the free metal Pd on the surface (Fig.4). The most intense peak, ca. 335.1–335.5 eV, was due to the emission from the 3d levels of the Pd metal, meaning that $Pd(hfa)_2$ was impregnated into the Kevlar® fabric and deposited onto the surface by thermal decomposition after 15 min treatment. The Pd concentration was about 1.27 at.%.

Electron probe X-ray microanalysis (EPMA) was performed on a JXA-8621MX (JEOL Co., Ltd.) to inspect the distribution of elements. The result of EPMA clearly indicates that the Pd catalyst was evenly distributed on the surface of the Kevlar® filament as shown in Fig.5.

The Kevlar fibers impregnated with Pd were electroless-plated in ATS-ADDCOPPER (Okuno Chemical Industry Co., Ltd.) mixture by a conventional method at 42±2 °C for 5–40 min by magnet stirring or under ultrasonic irradiation (Ultrasonic Cleaner Branson-3150 (Yamato Scientific Co., Ltd.)). After the plating process, the sample was dried in a vacuum dryer for 24 h.

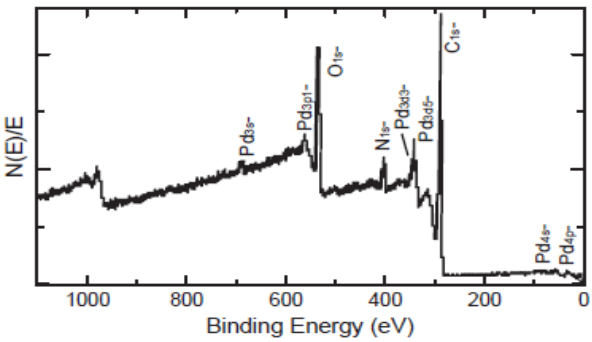

Fig.4 XPS survey spectra of Kevlar® fabric (T732) impregnation with $Pd(hfa)_2$ (1.0 wt%) at 150 °C and 15 MPa for 15 min.

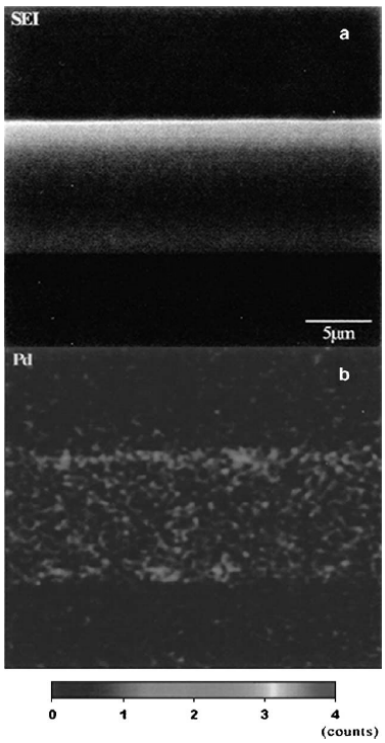

Fig.5 Surface image analysis of Kevlar®-29 fiber impregnation with $Pd(hfa)_2$ (1.0 wt.%) at 10 MPa and 150 °C for 15 min. (a) SEI (Secondary Electron Imaging) image, (b) EPMA image.

The surface morphology of the fiber plated was examined by a scanning electron microscope (SEM). The electric resistivity or the volume resistivity of the plated fabric was measured by the four-point probe method using a Roresta AP MCP-T400 (Mitsubishi Petrochemical Co., Ltd.). A PC500 Digital Multimeter (Sanwa Meter. Com.) was used to appraise the resistivity of the plated Kevlar®-29 fiber of a certain length. The electromagnetic shielding effectiveness was measured by the KEC (Kansai Electronic Industry Development Center) method [4,5]. A tape peel test referenced by the Japanese Industrial Standard (JIS H8504:15, 1999) was used to assess the adhesion of the

plating copper film on the Kevlar® sample.

The XPS analysis demonstrates that, along with the increasing amount of $Pd(hfa)_2$, more $Pd(hfa)_2$ were impregnated and pyrolyzed to the surface of the fiber, but

when the amount of $Pd(hfa)_2$ exceeded 2.0 wt.%, the concentration of Pd was close to equilibrium as shown in Fig.6. Moreover, as can be seen in the spectra (Fig.7), Pd peaks are less detected in the more superficial layer than in deeper region. The Pd is impregnated deeper into the fibers than the F which stays at the surface of the fibers,.

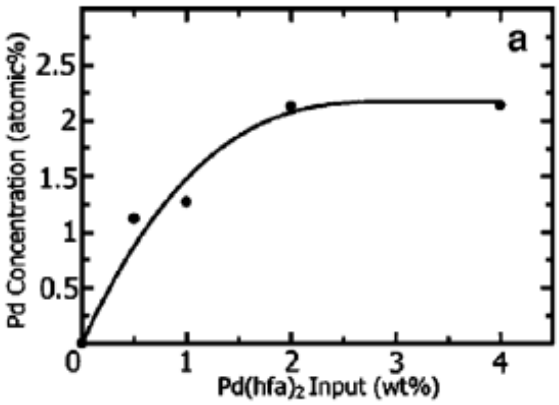

Fig.6 Effect of the amount of $Pd(hfa)_2$ on the Pd concentration. The $Pd(hfa)_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

In the same condition, the weight of the Cu coated onto the Kevlar® fabric within the same duration increased

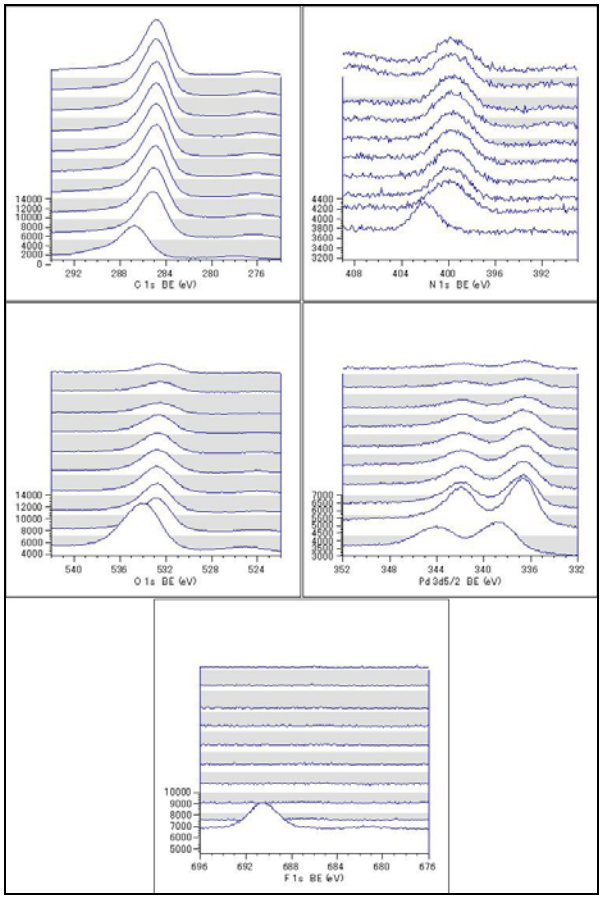

Fig.7 XPS depth profile for aramid fiber surface after SCF-Palladium (II)- hexafluoroacetylacetonate impregnation for 3 h and thermal treatment for 1 h showing the differences between the chemical shifts of C 1s, N 1s, O 1s, Pd 3d5/2, Pd 3d3/2, and F 1s atoms in the surface and deeper regions and the high detection of Pd peaks in depth regions.

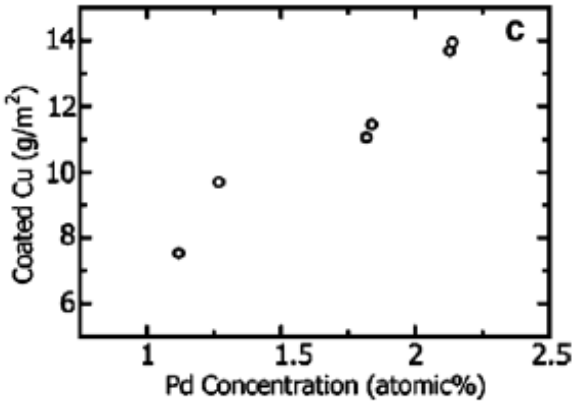

Fig.8 Effect of the Pd concentration on the amount of Cu coating after electroless copper plating under magnet stirring for 5 min at 42 °C. The $Pd(hfa)_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

corresponding to the increase of the Pd concentration (Fig.8). It shows that as the amount of the complex exceeds 2.0 wt%, the amount of Cu coating reaches at equilibrium because the catalytic agent on the fabric surface reaches in saturation.

Fig. 9 shows that at the same temperature and pressure during the supercritical pretreatment, the Pd concentration on the fabric surface subsequently increased along with the extension of the supercritical pretreatment time. Along with increasing time of the impregnation and heat treatment, more $Pd(hfa)_2$ were impregnated and pyrolyzed, which also means more activated Pd catalyst were deposited on the fabric surface.

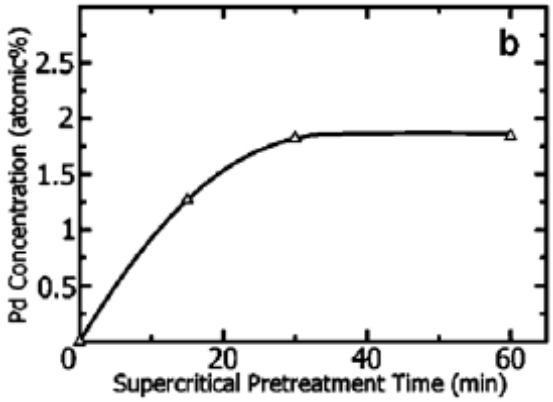

Fig.9 Effect of the supercritical pretreatment time on the Pd concentration. The $Pd(hfa)_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

By using KEC method, it was proved that the electromagnetic shielding effectiveness could reach 82–67 dB when ultrasonic irradiation was used, while 75–58 dB could be reached when magnet stirring was used in the frequency range of 10–1000 MHz, respectively. Moreover, Kevlar®-29 fiber impregnation with $Pd(hfa)_2$ (1.0 wt.%) at 10 MPa and 150 °C for 15 min, then plating under ultrasonic irradiation for 40 min at 42 °C resulted in the

electric resistance of 0.01 Ω /cm, and the volume resistivity reached 4.48×10^{-6} Ω ·cm.

In addition, the adhesion of the copper coating onto the Kevlar® fiber/fabric surface was excellent, as demonstrated by the results of a simple tape peel test. The copper coating did not peel off, and when an adhesive tape was firmly stuck onto the film and vigorously removed, no copper was observed on the tape. Such high adhesion of cupper plating on the fiber is caused by distribution of Pd, which is produced by reduction of Pd complexes diffused into fiber. The state of the Pd in Kevlar fiber is shown in Fig.10.

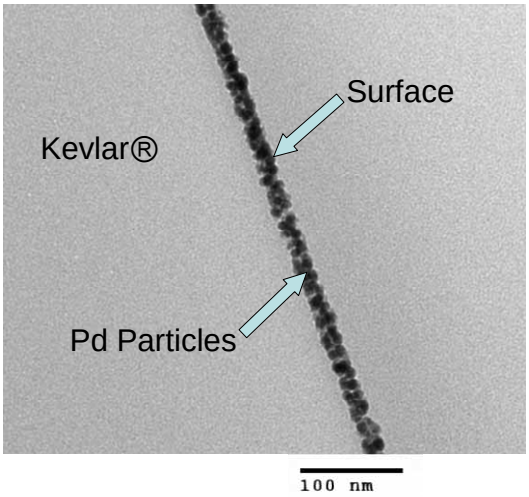

Fig.10 TEM image for cross-section of Pd-impregnated Kevlar fiber. Pd particles are distributed in the fiber.

Larger plants having 100 and 350 liter-treating bath were constructed to produce the functional fibers and textiles in market scale (Fig.11).

Fig.11 Practical supercritical fluid plant having 350 liters treating bath for fiber and textile treatments.

2.2 Impregnation of metal complex into aramid films and metal plating

Regarding the results previously explained, aramid films were impregnated with the organometallic complexes, $Pd(hfa)_2$ and palladium (II)-acetylacetonate ($Pd(acac)_2$) more stable at high temperature. The experimental conditions for the impregnation were 150 °C, 15MPa and respectively 30 minutes and 3 hours with a certain amount of complex. The impregnation and electroless copper plating processes were the same as those used to treat fibers.

According the first investigations, aramid films have more affinity with $Pd(acac)_2$ than $Pd(hfa)_2$. The plating of aramid films impregnated with $Pd(acac)_2$ is faster and led to an homogeneous and shiny copper layer on the surface of the films. Even after increasing the amount of $Pd(hfa)_2$, it was still not possible to have the same quality of plating.
To get an adhesion property as good as the one obtained for fibers, a thermal treatment (from 60 to 180 °C for 5 to 60 minutes) had to be added to the process before and/or after the electroless copper plating. This treatment prevented the action of the water contained in aramid films but also ensured reactions between the impregnated Pd and the films to get a better impregnation.
Those last experiments made possible to get an excellent adhesion, no metal remained on the adhesive tape after being peeled off. Moreover, they showed that the shorter the electroless copper plating is the better is the copper layer on the surface of the film. So the electroless copper plating time was decreased from 15 minutes to 40 seconds.

3. CONCLUSIONS

Applying the principle of supercritical fluid dyeing, some new textile processing has been investigated. Impregnation of functional polymers into fibers, the fixation of functional natural compounds on the textiles, the polymerization of functional monomers in the fibers and metal plating on the fibers and textiles were tested.

The new pretreatment method for electroless plating has only one stage, which is the impregnation of $Pd(hfa)_2$ or $Pd(acac)_2$ into Kevlar® fiber/fabric/films based on the high solubility of the hydrophobic $Pd(hfa)_2$ and $Pd(acac)_2$ in $scCO_2$. Simultaneously, the impregnated $Pd(hfa)_2$ or $Pd(acac)_2$ are activated by over-heating. After the supercritical pretreatment, the treated Kevlar® fiber/fabric/film is immersed in an electroless copper plating solution.

Such simple treatment using $scCO_2$ treatment process is expected to represent an eco-friendly alternative, as the number of stages is drastically reduced and no wastewater is generated.

4. ACKNOWLEDGEMENT

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