Application of supercritical carbon dioxide for textile processing

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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.

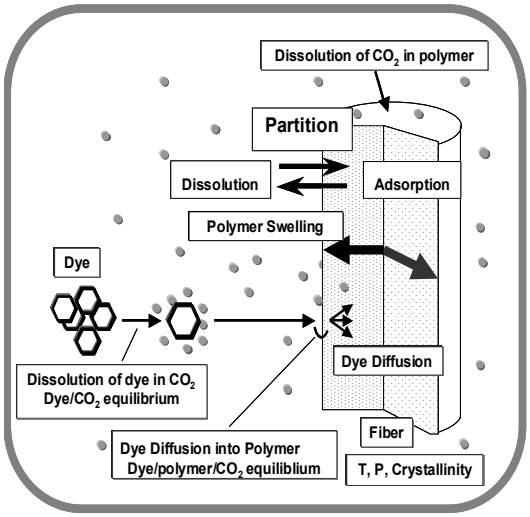

Fig.1 Mechanism of supercritical fluid dyeing (modified Schollmeyer's Model).

2. NEW APPROACH FOR TEXTILE PROCESSING

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 functional polymers into polyester fabrics using $scCO_2$

Poly(ethylene glycol) with molecular weight 1,000 (PEG 1,000) and silicon oil with molecular weight 5,000 (Silicon 5,000) were impregnated into polyester fabrics at 125°C and 25MPa from their $scCO_2$ solution, respectively. In the case of PEG 1,000, the equilibrium fixed amount was ca.0.6, and this was located uniformly in the PET fiber. PEG-impregnated PET fabric has good wettability against water. Silicon 5,000 was fixed 2.3 wt%, but the concentration of silicon near the surface was a little higher than middle of fiber. Silicon-impregnated fabric possessed extra high water repellent property.

2.2 Polymerization of pyrrol in $scCO_2$-expanded PET fibers

In order to give an anti-electrostatic property on PET fabric, also the supercritical fluid technique was applied; i.e.

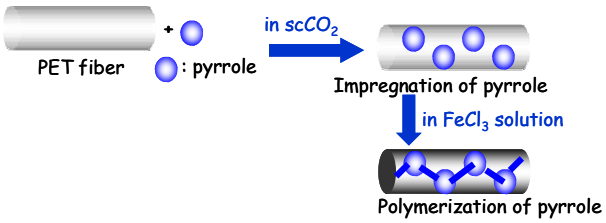

Fig.2 Preparation of conductive PET fabric by immersing of pyrrol and its polymerization.

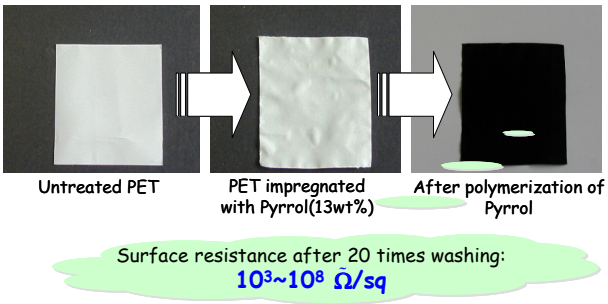

Fig.3 Appearance of PET fabric treated with pyrrol

much amount of pyrrol was impregnated into PET fabric in $scCO_2$. Pyrrol was then polymerized in PET fabric by immersing in aqueous solution of $FeCl_3$.(Fig.2). As result, enough amount of pyrrol (~13wt%) was impregnated into PET fabric using $scCO_2$ at 125□ and 15MPa for 30 min. After then the pyrrol-impreganted PET fabric was immersed in an aqueous $FeCl_3$ solution (x%) to polymerize (oxidized) pyrrol in the fabric. After treating in $FaCl_3$ solution the fabric became black (Fig.3) and high electric conductivity was obtained.

2.3 Impregnation of cross-linking agent into fibers and fixation of functional polymers on them

Some hydrophilic cross-linking agent having three reactive groups, for example cyanulchloride, which has relatively high solubility in $scCO_2$, can be easily impregnated into PET fabric (Fig.4). When the PET fabric impregnated with cross-linking agent is put in an aqueous sericin solution, sericin is reacted with cyanulchrolide in the PET fabric and fixed in the fabric. The washing fastness is very high. By such way the other proteins and polysuccharides were fixed on PET fabric to obtain hydrophilic property.

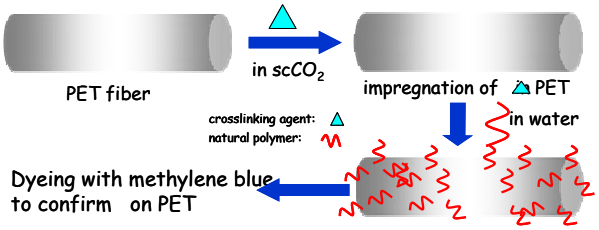

Fig.4 Impregnation of crosslinking agent into PET fiber and surface modification with natural polymers.

2.4 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

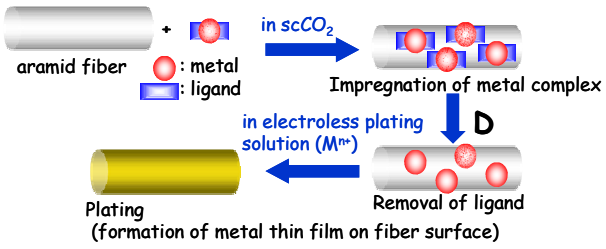

Fig.5 Process of electroless plating of aramid Fibers using $scCO_2$.

in a short time (Fig.5). 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.

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.6 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.

The Kevlar® samples impregnated with $Pd(hfa)_2$ in

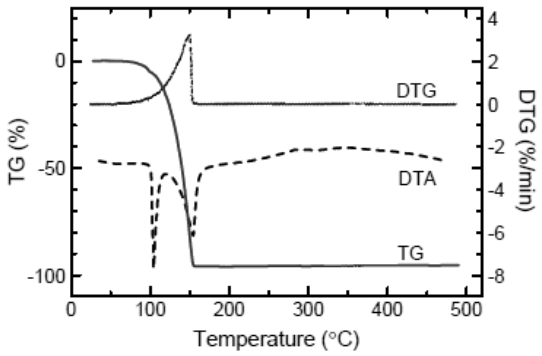

Fig.6 Combined thermogravimetric(TG), differential thermo-gravimetric (DTG), and differential thermal analytic (DTA) curves of $Pd(hfa)_2$ in a dynamic argon atmosphere.

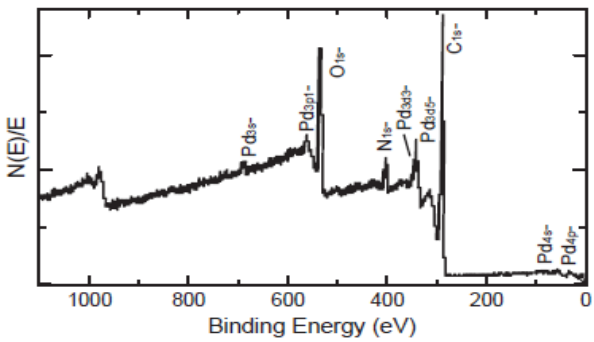

Fig.7 XPS survey spectra of Kevlar® fabric (T732) impregnation with $Pd(hfa)_2$ (1.0 wt%) at 150 °C and 15 MPa for 15 min.

$scCO_2$ 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.7). 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.8.

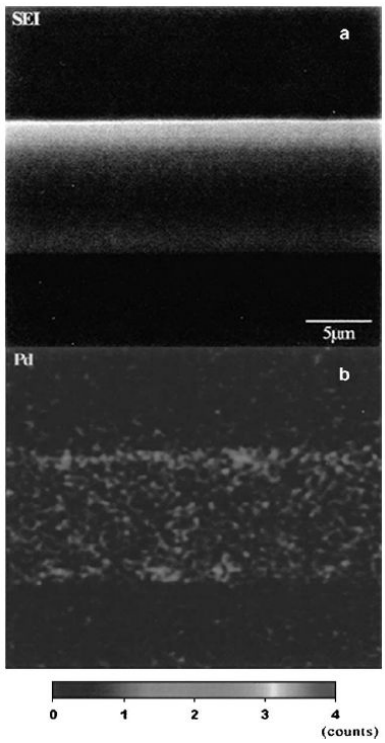

Fig.8 Surface image analysis of Kevlar®-29 fiber impregnation with $Pd(hfa)_2$ (1.0 wt.%) at 10 MPa and 150 °C for 15 min. (a) SEI (Secondary Electron Imaging) image, (b) EPMA image.

The 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.

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

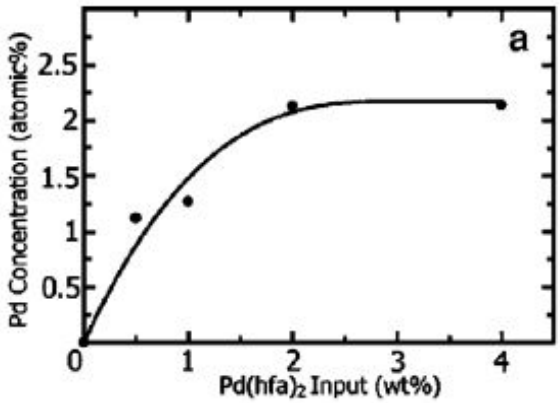

Fig.9 Effect of the amount of $Pd(hfa)_2$ on the Pd concentration. The Pd(hfa) $_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

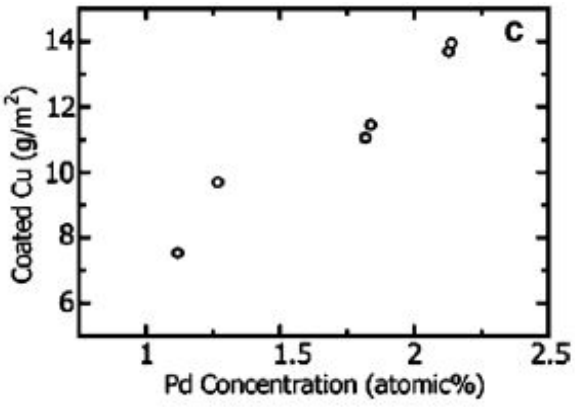

Fig.10 Effect of the Pd concentration on the amount of Cu coating after electroless copper plating under magnet stirring for 5 min at 42 °C. The Pd(hfa) $_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

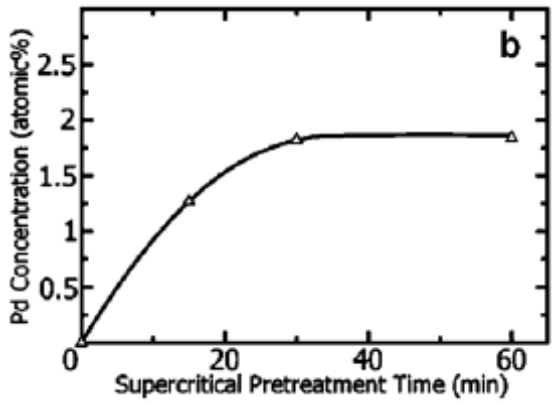

Fig.11 Effect of the supercritical pretreatment time on the Pd concentration. The $Pd(hfa)_2$ was impregnated into the Kevlar® fabric (T732) using $scCO_2$ at 150 °C and 15 MPa.

when the amount of $Pd(hfa)_2$ exceeded 2.0 wt.%, the concentration of Pd was close to equilibrium as shown in Fig.9.

In the same condition, the weight of the Cu coated onto the Kevlar® fabric within the same duration increased corresponding to the increase of the Pd concentration (Fig.10). 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. 11 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.

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.

Larger plants having 100 and 350 liter-treating bath were constructed to produce the functional fibers and textiles in market scale (Fig.12).

Fig.12 Practical supercritical fluid plant having 350 litter treating bath for fiber and textile treatments.

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 $Pd(hfa)_2$ into Kevlar® fiber/fabric based on the high solubility of the hydrophobic $Pd(hfa)_2$ in $scCO_2$. Simultaneously, the impregnated Pd $(hfa)_2$ is activated by over-heating. After the supercritical pretreatment, the treated Kevlar® fiber/fabric 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

The part of this work is supported by Ministry of Ecology, Trade and Industry (METI) and Ministry of Education , Culture, Sports, Science and Technology (MEXT), Japan.

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