초임계 이산화탄소를 이용한 구리 도금 전도성 섬유의 제조와 특성

조항진*, 호리 테루오, 타바타 이사오[1], 히사다 켄지, 히로가키 카즈마사
후쿠이대학교 공학대학원 응용섬유과, [1]후쿠이대학교 기술지원부
(c767980@freechal.com*)

Preparation and Characterization of Copper Plated Synthetic Fibers using Supercritical Carbon Dioxide

H. J. Cho*, T. Hori, I. Tabata[1], K. Hisada, K. Hirogaki
Department of Fiber Amenity Engineering, Graduate School of Engineering, Fukui University
[1]Technical Support Division, University of Fukui
(c767980@freechal.com*)

1. Introduction

Supercritical fluids have been used in many different fields ranging from classical extraction to sophisticated industrial processes which can only be justified by the high economic value of the find products. Until now, most fiber surface plating has been achieved by electroless metal plating. But the old electroless metal plating pretreatment process has many problems, such as the complicated abundance of stage, surface adjustment, and etching, etc.[1~3] It is now well known that supercritical carbon dioxide ($scCO_2$) is nether toxic nor flammable and is available at low cost, and can easily be recycled, and so on.[4,5] This article designed a new pretreatment process, in which the organometallic complex was impregnated into synthetic fibers by using $scCO_2$. The catalyst is formed at the fiber surface through the removal of the ligands by appropriate reduction treatments without using hydrogen, and the electroless metal plating can be conducted easily.

2. Experimental

2. 1. Method

PET(500d/96f) and Nylon6(420d/48f) fibers don't have twist. The processes of supercritical pretreatment, decompression, and electroless deposition of copper on synthetic fiber by magnet stirring are shown schematically in Fig. 1. The synthetic fibers were cut into 150cm, and tied

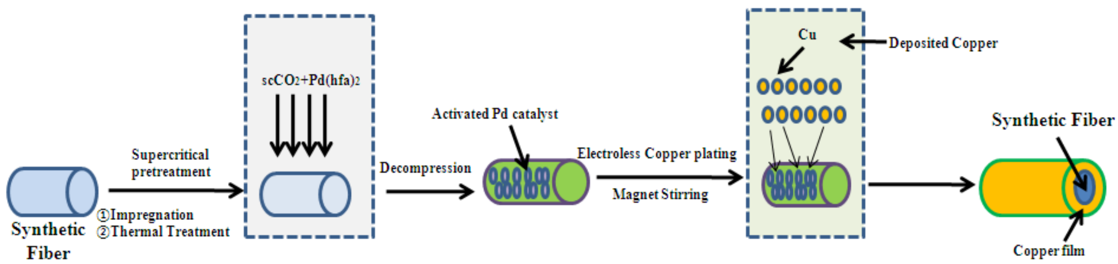

Fig. 1. Schematic illustration of the processes of supercritical pretreatment, decompression and electroless deposition of Cu on synthetic fiber by magnet stirring.

both ends of fiber to prevent from loosing mono-filaments. All experiments were performed on a batch-type supercritical extractor. Before sealing the sample cartridge, a glass filter was placed over and under the synthetic fibers.[6] A certain amount of Palladium(II) hexafluoro-acetylacetonate ($Pd(hfa)_2$) powder, calculated in 5wt.% of the weight of the sample fiber, was placed on the glass filter. After the desired temperature reached, the sealed sample cartridge was placed in the stainless steel vessel, and then carbon dioxide was added via the high pressure syringe pump to the desired pressure.

Synthetic fibers were dipped into the electroless copper plating solution at 42±2ºC for 30min under magnet stirring. The agitation of the mechanical stirring was set at about 200rpm. After the plating process, the samples were kept at room temperature for 24 hour in order to remove any moisture remaining on the fiber.

2. 2. Analysis

The structure of copper plated synthetic fibers was investigated using SEM and EMAX. Especially, EMAX can show dispersed copper on the fiber. For measurement of the electric characteristic, the conductivity of the synthetic fibers was measured at intervals of 10cm using Micro Ohm Meter. A friction testing device was designed.[7] Cu plated fibers were tightened a servomotor and 20g weight through 3 metal pins. And then, the synthetic fibers were reciprocated under regular speed (6πcm/2s) 50 and 100times. And Copper plated synthetic fibers were dipped into tap water for 1 hour in order to measure washing test. The agitation rate of the mechanical stirring was set at 700rpm with magnet stirrer, and the temperature at 50ºC. After abrasion and washing test, the surface structure and conductivity of the synthetic fibers were analyzed.

3. Results and Discussion

The conductivity (σ) was evaluated at room temperature. On the average, the conductivity of fiber is evaluated using volume resistance (Ω·cm) or sheet resistance (Ω/□) in comparison with other materials.[8] This study used volume resistance. Cross section areas of copper plated fibers, manufacturing under each temperature and time, were indicated in Table. 1. Cross section area is calculated from mass, length and density (Cu: 8.94g/cm^3, PET: 1.39g/cm^3, Nylon: 1.15g/cm^3).

Table. 1. Supercritical pretreatment for copper plated synthetic fibers and their characteristics.

Nylon					PET				
	$scCO_2$ pretreatment		characteristics of Cu plated fiber			$scCO_2$ pretreatment		characteristics of Cu plated fiber	
No.	Temp. (℃)	Time (min)	Cross section area ($\times 10^{-4} cm^2$)	Conductivity ($10^{-4}\Omega\cdot cm$)	No.	Temp. (℃)	Time (min)	Cross section area ($\times 10^{-4} cm^2$)	Conductivity ($10^{-4}\Omega\cdot cm$)
N1	120	20	4.548	35.212	P1	120	20	4.499	3.082
N2		40	4.472	30.074	P2		40	4.649	1.251
N3		60	4.509	20.948	P3		60	4.663	1.134
N4		100	4.538	5.788	P4		100	4.571	1.418
N5	130	20	4.518	30.581	P5	130	20	4.668	0.841
N6		40	4.496	21.574	P6		40	4.559	1.219
N7		60	4.713	3.508	P7		60	4.582	1.465
N8		100	4.749	2.161	P8		100	4.579	1.064
N9	140	20	4.545	16.569	P9	140	20	4.611	0.881
N10		40	4.727	1.824	P10		40	4.571	0.809
N11		60	4.725	1.348	P11		60	4.654	0.671
N12		100	4.878	0.732	P12		100	4.598	0.942
N13	150	20	4.504	13.524	P13	150	20	4.601	0.894
N14		40	4.692	1.217	P14		40	4.581	1.005
N15		60	4.809	0.985	P15		60	4.553	1.129
N16		100	4.762	0.881	P16		100	4.591	1.104

All pretreatments were tested under 150bar pressure. Table. 1. shows the good conductivities under $\times 10^{-4}\Omega\cdot cm$. PET fiber didn't largely change the conductivity by time and temperature. The best conductivity of PET fiber was $6.71\times 10^{-5}\Omega\cdot cm$ under sample no. P11 (Temperature: 140℃, Time: 60min). But, nylon fiber changed the conductivity by time and temperature. Generally, the conductivity of nylon fiber became better according to time and temperature increase. $Pd(hfa)_2$ quickly permeate into PET fiber.[8] But it spent over 40min to $Pd(hfa)_2$ permeate into nylon fiber completely. The best conductivity of nylon fiber was $7.32\times 10^{-5}\Omega\cdot cm$ under sample no. N12 (Temperature: 140℃, Time: 100min). In case of just thinking about plating copper under the best optimum condition, fiber's conductivity is ignored, the conductivity of plating copper on PET fiber (cross section area: $4.29\times 10^{-5} cm^2$) is $6.18\times 10^{-6}\Omega\cdot cm$ and the conductivity of plating copper on nylon fiber (cross section area: $5.31\times 10^{-5} cm^2$) is $7.96\times 10^{-6}\Omega\cdot cm$. These results are closed to original copper conductivity ($1.71\times 10^{-7}\Omega\cdot cm$). After supposing copper was coated on mono-filament evenly, the thickness of copper was calculated. Copper's thickness of sample no. P11 was around 600nm surrounding mono-filament (about 5denier). This result shows copper's thickness is very thin, so copper plated fiber still keeps the flexibility of fiber but also has good conductivity. Meanwhile, a melting point becomes lower under supercritical state, but the normal melting point of $Pd(hfa)_2$ is 140℃. For the this reason, conductivities of PET and nylon fiber were better over 140℃.

For the washing test, sample no. P15 and N15 were selected. Washing test was repeated 10 times. The conductivity after washing test became lower, but this result is from damage of mono-filament rather than break or drop plating copper. PET fiber shrank and mono-filaments are gathered each other under high temperature, but mono-filaments of nylon were not stable. Hence, PET fiber bore better than nylon fiber from washing test.

Normally, abrasive test of fiber is measuring number of reciprocation between fiber and friction device until fiber cutting. But this method is mainly reflected in mechanical properties

Table. 2. Conductivities of copper plated synthetic fiber using supercritical carbon dioxide before and after washing and abrasion test.

Conductivity($\times 10^{-4}\Omega\cdot cm$)				
	PET fiber		Nylon fiber	
	Before	After	Before	After
Washing test	0.889	0.989 (5times) 1.438 (10times)	0.973	3.852 (5times) 14.902 (10times)
Abrasion test	0.957	8.168 (50cycles) 13.264(100cycles)	1.287	43.387 (50cycles) 110.998(100cycles)

of original fiber instead of coating material's properties. Therefore, for investigating abrasion property of coating material, the method of measuring conductivity and surface condition was used after rubbing fiber with pins at constant time. This method can't only evaluate abrasion property, but also adhesive strength between fiber and coating material. For the abrasion test, sample no. P11 and N11 were selected. Copper plated synthetic fiber after washing and abrasion test had good conductivities as ever. The conductivity after abrasion and washing test is displayed in Table. 2.

4. Conclusions

In this study, copper plated synthetic fibers were produced after impregnating $pd(hfa)_2$ under different temperature and time to make conductive fiber using supercritical carbon dioxide. The optimum condition was sample no. P11 (Temperature: 140℃, Time: 60min) and N12 (Temperature: 140℃, Time: 100min). These synthetic fibers had excellent conductivities (P11: $6.71\times10^{-5}\Omega\cdot cm$, N12: $7.32\times10^{-5}\Omega\cdot cm$) and plated copper has about 600nm thickness so, still keep good flexibility. Also, copper plated synthetic fibers had good conductivities, even though stood against abrasion and washing. For these reasons, copper plated synthetic fiber using $scCO_2$ can apply for many fields, such as E-textile and smart textile, etc.

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