Polymer Surface Metallization using Carbon Dioxide Supercritical Fluid and Thermal Treatment

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1. ABSTRACT

Polymer fiber surfaces were metallized by means of CO_2 supercritical fluid followed by thermal treatment. Pd metal complex was loaded onto the polymer substrate to activate the copper deposition by electroless plating. Thermal treatment diffused the metal complex seeded onto fiber to sub-surface regions and in this way adhesion strength between substrate and metal layer was greatly improved. Since the uniformity of copper deposited onto fiber was enhanced, low electrical resistivity conductive fibers were obtained. XPS analyses confirmed the deeper penetration of metal into substrate surfaces.

2. INTRODUCTION

The use of supercritical fluids (SCF) to modify polymer surfaces followed by electroless plating is being appraised around the world due to these techniques enable the metal coating of thermoplastics and irregular surfaces. Ober et.al. has recognized the importance of this technology in a recent publication where the $scCO_2$ applications in microelectronics processing is highlighted. According to this, $scCO_2$ technologies are proposed for microelectronic applications in response to needs for low chemical-use processes, material-compatible cleaning systems, etc. Also, in response to increase in regulations on the release of toxic chemicals, costs of water and solvent use, the semiconductor industry is eager to abate chemical and water usage in production processes [1].

In the last years our lab has been focused in the development of conductive fibers and films [2-4]. Herein, the effectiveness of this method for polymeric surface metallization is reported.

3. EXPERIMENTAL

All experiments, for 50-cm-long samples, were conducted on a batch-type supercritical extractor (SFE System 2000, ISCO, USA). Details of the experimental procedure, apparatus and chemicals employed are given elsewhere [2-4]. The electrical resistivity of coated fiber was measured using a 7½ Digit Nano Volt / Micro Ohm Meter from Agilent Co (Tokyo, Japan). XPS analyses were performed on a JEOL 9010 MCY-XPS X-ray photoelectron spectrometer, using monochromatic Mg Kα radiation (hv = 1253.6eV) operated at 10 kV and 10 mA.

4. RESULTS AND DISCUSSION

Aramid fibers were treated at low temperature and the results compared to previous data at higher temperature. The results are shown in Table 1.

Table 1. Qualitative evaluation of adhesive strength of copper layer into the aramid fiber under various $scCO_2$-treatment and thermal treatment times at set temperature after various plating times.

Experimental Conditions		Electrical Resistivity (R) and Adhesion (Ad) Results at different conditions					
		Plating A		Plating B		Plating C	
IT (h)	TT (h)	R	Ad	R	Ad	R	Ad
0.5	0	3.3	ng	2.3	ng	1.5	ng
	1	1.5	g	1.5	mol	1.1	vg
	2	2.1	vg	1.4	mol	1.2	vg
1	0	2.7	ng	2.3	ng	2.2	ng
	1	1.8	mol	1.5	g	1.1	vg
	2	1.6	g	1.2	g	1.2	vg
2	0	2.5	ng	1.6	ng	1.6	ng
	1	1.6	g	1.3	vg	1.1	vg
	2	1.6	g	1.3	g	1.1	vg
3	0	1.8	ng	1.8	mol	1.9	ng
	1	1.4	vg	1.4	vg	1.1	vg
	2	1.7	g	1.5	vg	1.1	g
4	0	2.1	ng	1.8	mol	1.6	ng
	1	1.6	g	1.3	vg	1.2	g
	2	1.9	ng	1.3	vg	1.2	mol
5	0	2.4	ng	1.5	ng	1.6	ng
	1	1.6	g	1.2	g	1.1	g
	2	1.7	mol	1.3	g	1.1	vg
6	0	1.5	ng	1.6	ng	1.3	mol
	1	1.5	g	1.2	g	1.2	mol
	2	1.2	g	1.1	g	0	0

IT = impregnation time; TT = thermal treatment; Plating A, B and C = 20, 25 and 30 min, respectively. Adhesion: vg = very good, g = good, mol = more or less, ng = not good.

Also, the XPS results for Pd relative atomic composition (%) detected in the aramid surface and its sub-surface after 3 h of metal complex impregnation under low and high temperature, and without and with thermal treatment are indicated in Table 2. The results suggest the possibility of treat aramid fibers under lower temperature conditions.

Table 2. Comparison between relative atomic composition (%) in the aramid surface at low and high temperature.

IT (℃)	TTt (h)	Etch	Pd/N
130	0	0	0.20
150	0	0	0.21
130	0	1	0.27
150	0	1	0.31
130	1	0	0.23
150	1	0	0.22
130	1	1	0.29
150	1	1	0.33

IT = impregnation temperature; TTt = Thermal treatment time

PET fibers were also treated with successful results. Cu-coated PET fibers showed low resistivity and enhanced adhesive strength. Fig. 1 shows the XPS detection of Pd in PET fiber surface after different SCF-temperatures and similar thermal treatment time.

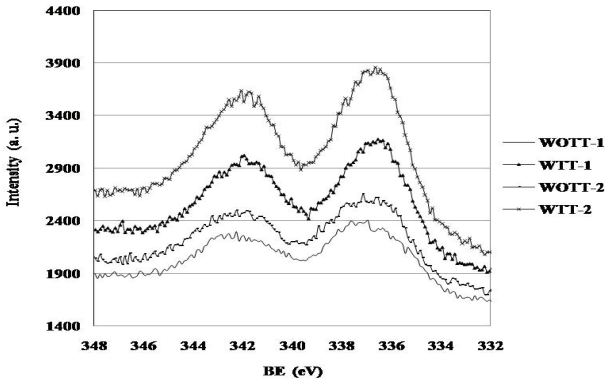

Fig. 1. XPS narrow spectrum showing the Pd peaks detected in the surface of PET fibers without thermal treatment (WOTT) and with thermal treatment (WTT).

5. SUMMARY

$ScCO_2$ followed by thermal treatment has been successfully challenged at lower temperature for development of conductive polymers like aramid fibers. Also, Cu-coated PET fibers showed low resistivity and enhanced adhesive strength. Thermal treatment is undoubtedly an excellent aid to diffuse Pd complex loaded onto thermoplastic surface and makes it moderately hydrophilic allowing uniform metal deposition during plating. XPS analysis confirmed that heating induced deeper diffusion of Pd and the existence of more Pd in the sub-surface. Finally, the effectiveness of this method for polymeric surface metallization has been proved.

6. REFERENCES

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