

NOTE

Studies on the Preparation and Properties of Conductive Polymers. VI. Two-Stage Method to Prepare Metallized Polymer Films

INTRODUCTION

Sumita et al. and Higashi et al.¹⁻² have shown that the surface electrical conductivities of films of poly(vinyl alcohol)-Cu²⁺ and polyacrylamide-Cu²⁺ were increased by doping iodine in acetone solution over the film surfaces. After iodine treatment, a whitish substance was found and was identified as γ -CuI, which was believed to be responsible for the enhanced electrical conductivity. In the previous papers of this series,³⁻⁷ a novel method was found, by which metallized polymer films were prepared from poly(vinyl alcohol) (PVA), polyacrylamide (PAAm), polyamide, polyurethane (PU), and polyacrylonitrile (PAN). These polymer metal chelate films exhibited low surface resistivity when reduced by metal-hydride reducing agents,^{3,4,6} heat treatment,⁷ or the re-plotting out method.⁵ The surfaces of these reduced-polymer chelate films were metallized by means of x-ray and ESCA analysis.

In this investigation, the two-stage method for preparing metallized polymer films is reported. In the first stage, PVA-AgNO₃ chelate films were treated with doping agents, such as an ethanol solution of I₂, an aqueous solution of K₂CO₃, or K₂CrO₄. Silver salts were formed on the film surfaces. In the second stage, these treated films were further reduced by a NaBH₄ aqueous solution. After these two stages of treatment, good electrical conductivity and films with long-term stability can be obtained. Similarly, PAN-AgNO₃ complex films were also investigated in this study.

EXPERIMENTAL

Preparation of Metallized PVA Films by the Two-Stage Method

PVA-AgNO₃ chelate films were prepared by the method reported in the previous paper of this series.³ Metallized PVA films were prepared by the two-stage method. In the

first stage, 25 wt % PVA-AgNO₃ chelate films (wt % AgNO₃ based on PVA weight) were dipped into a 6 wt % ethanol solution of I₂, a 10 wt % K₂CO₃ aqueous solution, or a 10 wt % K₂CrO₄ aqueous solution at room temperature for about 5 sec, respectively. These treated films were washed with ethanol or water and were dried at 100°C for 5 min. In the second stage, these dried films were dipped into a 0.6 wt % NaBH₄ aqueous solution at room temperature for about 20 sec. They were then washed with water and dried at 100°C for 15 min. The metallized PVA film was obtained.

Preparation of Metallized PAN Films by the Two-Stage Method

Commercial PAN fibers (3.0 g) were dissolved in N,N-dimethylformamide (DMF) (18 mL), and silver nitrate (0.75 g) was added directly into the PAN solution. The solution was stirred at 50°C for 72 h, its color changing gradually from colorless to dark brown. After cooling to room temperature, the solution of PAN-AgNO₃ complex was spread on dry glass plates with a gardener's knife. The glass plates were placed in a static air oven at 135–155°C for 30 min. PAN-AgNO₃ complex films were obtained.

In the first stage, PAN-AgNO₃ complex films were placed in a reflux ethanol solution of I₂ (6 wt %) for 6 h. These treated films were washed with ethanol and were dried at 100°C for 5 min. In the second stage, these dried films were dipped into a 3.0 wt % NaBH₄ aqueous solution at 65°C for 20 sec, then were washed with water and were dried at 100°C for 15 min. The metallized PAN film was obtained.

Electric Measurement

The surface electrical conductivities of the treated and reduced films were measured according to the conventional, four-terminal method, using aluminum foil electrodes, as described in the previous paper.²

Table I Effect of Doping Agents and Reducing Agents on the Surface Resistivity of PVA-AgNO₃ Chelate Films

First Stage		Second Stage	
Doping Agents	Surface Resistivity (Ω/cm ²)	Reducing Agents	Surface Resistivity (Ω/cm ²)
I ₂ /EtOH (6 wt %)	4.30 × 10 ⁴	NaBH ₄ (1 wt %)	3.0 × 10 ⁰
K ₂ CO ₃ Aq. (10 wt %)	1.34 × 10 ⁵	NaBH ₄ (1 wt %)	3.7 × 10 ⁰
K ₂ CrO ₄ Aq. (10 wt %)	1.70 × 10 ⁵	NaBH ₄ (1 wt %)	3.1 × 10 ⁰

X-Ray Analysis

X-ray diffraction patterns of the treated and reduced films were measured by a Shimadzu XD-3A diffractometer, using Cu Kα radiation generated at 30 KV and 20 mA.

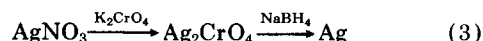
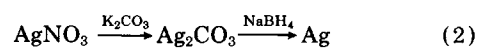
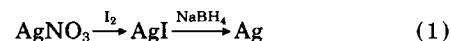
RESULTS AND DISCUSSION

Effect of Doping Agents and Reducing Agents on the Surface Resistivity of PVA-AgNO₃ Chelate Films

Metallized polymer films were prepared by a two-stage method in this study. In the first stage, PVA-AgNO₃ chelate films were treated with doping agents, such as an ethanol solution of I₂, an aqueous solution of K₂CO₃, or K₂CrO₄, respectively. These films showed surface resistivity in the range of 10⁴-10⁵ Ω/cm², as shown in Table I. These treated films were further reduced by an NaBH₄ aqueous solution in the second stage and they exhibited low surface resistivity around 10⁰ Ω/cm², as shown in Table I.

X-Ray Analysis

The PVA-AgNO₃ chelate films were treated with doping agent and reducing agent: the change of the surface substance on the films has been proposed as reflected by the following equations:



In order to confirm that the change of surface substance on the films is exactly as the equations mentioned above, these films were examined by means of x-ray diffraction.

As shown in Tables II-IV, the PVA-AgNO₃ chelate films were treated with doping agents in the first stage, such as an ethanol solution of I₂, an aqueous solution or K₂CO₃, or K₂CrO₄; the treated films clearly demonstrated that the main products on the film surfaces were silver salts, such as AgI, Ag₂CO₃, or Ag₂CrO₄. Subsequently, the

Table II Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-Ray Analysis for PVA-AgNO₃ Chelate Films Treated with I₂/EtOH Solution and Subsequently with NaBH₄ Aqueous Solution

Peaks	Film A ^a Experiment		Pure AgI Reference		Film B ^b Experiment		Pure Ag Reference	
	2θ	d	2θ	d	2θ	d	2θ	d
1	22.1	4.020	22.32	3.980	38.2	2.354	38.14	2.359
2	23.6	3.770	23.71	3.750	44.2	2.047	44.33	2.043
3	25.1	3.540	25.35	3.510	64.6	1.442	64.50	1.445
4	39.0	2.307	39.20	2.296	77.5	1.231	77.61	1.230
5	42.4	2.130	42.63	2.119				
6	46.1	1.967	46.31	1.959				

^a Film A prepared from PVA-AgNO₃ chelate film treated with I₂/EtOH solution only.

^b Film B prepared from Film A reduced by NaBH₄ aqueous solution.

Table III Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-Ray Analysis for PVA–AgNO₃ Chelate Films Treated with K₂CO₃ Aqueous Solution and Subsequently with NaBH₄ Aqueous Solution

Peaks	Film C ^a Experiment		Pure Ag ₂ CO ₃ Reference		Film D ^b Experiment		Pure Ag Reference	
	2θ	d	2θ	d	2θ	d	2θ	d
1	33.8	2.650	33.6	2.660	38.3	2.348	38.14	2.359
2	32.8	2.774	32.5	2.756	44.4	2.039	44.33	2.043
3	18.6	4.776	18.5	4.784	64.6	1.442	64.50	1.445
4					77.6	1.29	77.61	1.230

^a Film C prepared from PVA–AgNO₃ chelate film treated with K₂CO₃ aqueous solution only.

^b Film D prepared from Film C reduced by NaBH₄ aqueous solution.

silver salts on the treated film surfaces were reduced to metallic Ag when these films were further reduced by an NaBH₄ aqueous solution in the second stage. As shown in Tables II–IV, the results of x-ray analysis were in good agreement with standard samples. The above results indicate that the change of surface substance on the film was exactly as the equations mentioned above.

Silver metallized PAN film, using the PAN–AgNO₃ complex after heat treatment, has been reported in one of our previous papers.⁷ When PAN–AgNO₃ complex wet films were placed in a static air oven at 135–155°C for 2.0 h, definite silvery films were obtained. In this investigation, a two stage method was used, instead of heat treatment, for preparing silver metallized PAN films. PAN–AgNO₃ complex wet films were placed in a static air oven at 135–155°C for only 30 min rather than 2.0 h. The drying time was only 30 min in order to prepare PAN–AgNO₃ complex film rather than metallized film. In the first stage, the PAN–AgNO₃ complex film was treated with a refluxed ethanol solution of I₂ in order to form AgI on the film

surface. Then, in the second stage, the film treated with AgI on its surface was reduced to metallic Ag by an NaBH₄ aqueous solution. The reduced films exhibited the low surface resistivity of $2.8 \times 10^1 \Omega/\text{cm}^2$.

Silver metallized PAN film cannot be obtained when the PAN–AgNO₃ complex film was treated with an NaBH₄ aqueous solution directly. This might be explained if the AgNO₃ in the complex film cannot diffuse out and into the aqueous solution of NaBH₄. When the PAN–AgNO₃ complex film was placed in a refluxed ethanol solution of I₂, AgNO₃ in the complex film can diffuse out at a higher temperature and can react with I₂ to form AgI on the film surface. Then, AgI can be reduced easily into metallic Ag by using the NaBH₄ aqueous solution. Therefore, when polymer metal chelate films cannot be metallized by a one step process, such as reduction by metalhydride or a retroplating out method, the two-stage method to prepare metallized polymer films might be utilized. The proposed structure of PAN–AgNO₃ complex can be explained by ESCA analysis and will be reported in the future.

Table IV Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-Ray Analysis for PVA–AgNO₃ Chelate Films Treated with K₂CrO₄ Aqueous Solution and Subsequently with NaBH₄ Aqueous Solution

Peaks	Film E ^a Experiment		Pure Ag ₂ CrO ₄ Reference		Film F ^b Experiment		Pure Ag Reference	
	2θ	d	2θ	d	2θ	d	2θ	d
1	31.3	2.885	31.36	2.850	38.1	2.360	38.14	2.359
2	30.4	2.938	30.41	2.937	44.3	2.043	44.33	2.043
3	44.2	2.047	44.07	2.053	64.4	1.446	64.50	1.445
4					77.5	1.231	77.61	1.230

^a Film E prepared from PVA–AgNO₃ chelate film treated with K₂CrO₄ aqueous solution only.

^b Film F prepared from Film E reduced by NaBH₄ aqueous solution.

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