Studies on the Preparation and Properties of Conductive Polymers. VIII. Use of Heat Treatment to Prepare Metallized Films from Silver Chelate of PVA and PAN

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SYNOPSIS

Metallized polymer films were prepared from polyacrylonitrile or poly(vinyl alcohol) silver chelate solution by heat treatment. These metallized film exhibited low surface resistivity around 10^0 Ω/cm^2. The surface of these conductive films was proved to be metallized using X-ray analysis. The metal adhered on the film was believed to be responsible for the improvement of electrical conductivity. The effects of types and concentrations of silver salt, types and volume of solvent, and drying time on the conductivity of metallized films were investigated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

There are some reports that the polymerization of acrylonitrile can be accelerated by silver nitrate.[1,2] When a polyacrylonitrile (PAN) film prepared by this method was treated with reducing agents (hydrogen sulfide or halogen acid), the silver nitrate in the film was reduced or converted into silver, silver sulfide, or silver halide and migrated to the surface. The low surface resistivity of PAN was determined,[2] but other properties were not investigated.

Other reports discussed the doping of polyamic acids with electropositive metal salts.[3-9] The metal cation was reduced to the metal during a cure cycle to obtain metal-doped polyimide films. The authors found substantial increases in conductivity as compared to undoped polyimide films. In some cases, silver or palladium mirrors formed on the polymer surface.

In the previous articles of this series, metallized polymer films were prepared from polymer metal chelate films.[10-13] The polymer metal chelate films were prepared by metal salts mixed with polymers containing functional groups such as poly(vinyl alcohol) (PVA), polyamide, polyamide–imides (PAI), and polyurethane (PU). These polymer metal chelate films were reduced by reducing agents. Excellent conductive films with long-term stability were obtained.

In this study, instead of reducing agents used in the previous work, the effect of heat treatment was investigated. PVA and PAN metal chelate solutions with different concentrations of silver salts were prepared and reduced to metallized polymer films by heat treatment. The metallized substance on the surface of films as well as their surface resistivities were also examined.

EXPERIMENTAL

Preparation of PVA and PAN Silver Chelate Solution

$AgNO_2$ was added directly to a 10% (by weight) PVA water solution and $AgNO_3$ or $AgNO_2$ were added directly to PAN/DMF (N,N-dimethylformamide) solution; these given conditions are listed in Tables I–III. Solutions of these mixtures were stirred at 80°C for 20 min. The PVA or PAN silver chelate solutions were obtained.

Table I **Effect of the Amount of Silver Nitrate and The Volume of Solvent on the Conductivity of PAN/AgNO₃ Chelate Films Reduced by Heat Treatment**

Run No.	PAN (g)	AgNO$_3$ (g)	W^a (%)	Solvent	Solvent Volume (mL)	Concn^b (%)	Drying Time (°C)	Drying Time (h)	Surface Resistivity (Ω/cm^2)
1	3	0.75	25	DMF	18.0	15.0	135	2	1.0×10^0
2	3	0.75	25	DMAc	18.0	15.1	145	2	1.2×10^0
3	3	0.75	25	DMSo	18.0	13.2	155	2	1.8×10^0
4	3	0.60	20	DMF	18.0	15.0	135	2	1.5×10^0
5	3	0.60	20	DMF	45.0	6.6	135	12	$> 2 \times 10^7$
6	3	0.60	20	DMF	98.0	3.1	135	48	$> 2 \times 10^7$
7	3	0.36	12	DMF	18.0	15.0	135	2	2.0×10^0
8	3	0.30	10	DMF	18.0	15.0	135	2	$> 2 \times 10^7$
9	3	0.15	5	DMF	18.0	15.0	135	2	$> 2 \times 10^7$

^{a} $W\% = [\text{AgNO}_3 \text{ (g)}/\text{PAN (g)}] \times 100\%$.
^{b} Concentration (%) = [PAN (g)/(PAN (g) + solvent (g))] $\times$ 100%.

Preparation of Metallized Films by Heat Treatment

The resulting viscous PVA and PAN silver chelate solutions were cast onto clean poly(methyl methacrylate) plates and glass plates with a gardener's knife individually. The PVA–AgNO₂ chelate solutions on poly(methyl methacrylate) plates were heated in an oven at 60°C for 7 h. The PAN/AgNO₃ and PAN/AgNO₂ chelate solutions on glass plates were heated at 70°C for 7 h. These films were then peeled off and cut into test pieces of size 1 × 3 cm.

Electric Measurement

The surface electrical conductivity of the films was measured according to the conventional four-ter-

minal method using aluminum foil electrodes, as described in a previous article.[14]

Instrument Analysis

Visible and UV absorption spectral data of the polymer metal chelate solution were obtained by using a Jasco Model 7800 spectrophotometer. X-ray diffraction patterns of metallized PVA and PAN films were measured by a Shimadzu XD-3A diffractometer using CuKα radiation generated at 30 kV and 20 mA.

RESULTS AND DISCUSSION

Visible and UV Spectra Observations

The formation of a polymer metal chelate can be identified from both the color changes of the solution and the UV-visible spectra of the polymer solution

Table II **Effect of the Amount of Silver Nitrite on the Conductivity of PAN/AgNO₂ Chelate Films Reduced by Heat Treatment**

PAN (g)	AgNO$_2$ (g)	W^a (%)	Surface Resistivity (Ω/cm^2)
3	0.30	10	1.1×10^0
3	0.25	8.3	1.8×10^0
3	0.20	6.6	1.5×10^0
3	0.15	5	1.6×10^0
3	0.12	4	2.8×10^0
3	0.1	3.3	$> 2 \times 10^7$
3	0.05	1.67	$> 2 \times 10^7$

^{a} $W\% = [\text{AgNO}_2 \text{ (g)}/\text{PAN (g)}] \times 100\%$.

Table III **Effect of the Amount of Silver Nitrite on the Conductivity of PVA/AgNO₂ Chelate Films Reduced by Heat Treatment**

PVA (g)	AgNO$_2$ (g)	W^a (%)	Surface Resistivity (Ω/cm^2)
5	0.5	10	1.5×10^0
5	0.4	8	1.1×10^0
5	0.3	6	2.1×10^0
5	0.2	4	2.4×10^0
5	0.1	2	$> 2 \times 10^7$

^{a} $W\% = [\text{AgNO}_2 \text{ (g)}/\text{PVA (g)}] \times 100\%$.

or film. The formation of PVA–AgNO₃ chelate identified from UV-visible spectra was reported in our previous article.[10] In this study, the formation of $PVA–AgNO_2$, $PAN–AgNO_2$, and $PAN–AgNO_3$ chelate can also be identified from the color changes of solution and UV-visible spectra. When silver nitrite was added to the PVA solution and stirred for 20 min at 80°C for 20 min, this pale green mixed solution changed to dark brown. Similarly, the color of $PAN–AgNO_2$ and $PAN–AgNO_3$ solutions became dark brown. Lower stir temperatures can be used, but then a longer stir time is required for the formation of polymer metal chelate. The UV-visible spectra of the $PAN–AgNO_3$ solution shows absorption at 399 nm. From the above result, it is recognized that a chelate was formed by silver ions with PAN.

When $PAN–AgNO_2$, $PAN–AgNO_3$, and $PVA–AgNO_2$ chelate solutions were dried in an oven, both silver mirrors and/or thin film silver conductors were formed. The films, when removed from the glass plate [or the poly(methyl methacrylate) plate], showed noticeably different surfaces on the air and glass sides [or the poly(methyl methacrylate) side] (during heat treatment). Thus, the film from the glass side [or the poly (methyl methacrylate) side] was dark brown in appearance and was nonconductive, whereas that the air side was definitely silver metallic in appearance and possessed excellent conductivity. Reheating films removed from the glass plate [or the poly(methyl methacrylate) plate] but which had subsequently been in contact with air led to them becoming metallic in appearance and exhibiting good conductivity. The presence of oxygen during the heat treatment appears to be crucial, since the $PVA–AgNO_2$, $PAN–AgNO_2$, and $PAN–AgNO_3$ chelate solutions do not

Table IV   Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for PVA/AgNO₂ Chelate Films Reduced by Heat Treatment

Peaks	Films Aª Experiment		Pure Ag Reference	
	2θ	d	2θ	d
1	38.2	2.354	38.14	2.359
2	44.4	2.039	44.33	2.034
3	64.6	1.442	64.50	1.445
4	77.6	1.229	77.61	1.230

ª Film A prepared from PVA/AgNO₂ chelate films reduced by heat treatment.

Table V   Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for PAN/AgNO₂ Chelate Films Reduced by Heat Treatment

Peaks	Films Bª Experiment		Pure Ag Reference	
	2θ	d	2θ	d
1	38.2	2.354	38.14	2.359
2	44.3	2.043	44.33	2.034
3	64.6	1.442	64.50	1.445
4	77.5	1.231	77.61	1.230

ª Film B prepared from PAN/AgNO₂ chelate films reduced by heat treatment.

give rise to metallic surfaces when heated either in an atmosphere of dry nitrogen or in a vacuum.

To determine the optimal PAN/AgNO₃/DMF ratio needed to obtain the electric-conducting film, several experiments were carried out in which the volume of DMF was changed while the same PAN/AgNO₃ weight ratio was maintained. The results are shown in the Table I. The following trends were observed: (1) When too much solvent (DMF) was added, evaporation of the solvent during the heat treatment prevented oxygen from reaching the PAN surface and no reduction appeared to occur as shown in runs no. 5 and 6 of the Table I; (2) when the films were too thin, owing to the evaporation rate during the heat treatment being too fast, the surface of films was insufficiently in contact with oxygen. Then, the surface was nonmetallic and nonconductive. Therefore, oxygen was crucial for production of electric-conducting films.

There are no substantial changes in the conductivity, as shown in runs no. 1, 2, and 3 in the Table I (surface resistivity 1.0–1.8 Ω/cm^2), indicating that the effect of solvent (DMF, DMAc, DMSO) on the conductivity is insignificant. Parameter W is the ratio of the weight of silver nitrate to that of weight of the PAN. Good conductivity is obtained (see Table I, runs no. 1, 4, and 7) when the value of W is between 12 and 25%. Similarly, when the value of W is between 4 and 10% for $PAN–AgNO_2$ and $PVA–AgNO_2$ chelate film, low surface resistivity is obtained, as shown in Tables II and III. The way in which the different anions in the silver salt, such as silver sulfate, silver acetate, and silver perchlorate, affected the conductivity was investigated under the same W value of 0.08 of PAN/Ag^+ film; favorable results were not obtained. The surface resistivity of PAN film was more than 2×10^7 Ω/cm^2. Both the

Table VI Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for PAN/AgNO₃ Chelate Films Reduced by Heat Treatment

Peaks	Films C[a] Experiment		Pure Ag Reference	
	2θ	d	2θ	d
1	38.2	2.354	38.14	2.359
2	44.2	2.047	44.33	2.034
3	64.4	1.446	64.50	1.445
4	77.6	1.229	77.61	1.230

[a] Film C prepared from PAN/AgNO₃ chelate films reduced by heat treatment.

nitrate ion and nitrite ion of the PAN/Ag⁺ chelate were effective for conduction. But for the PVA/Ag⁺ chelate film, only the nitrite ion of the PVA/Ag⁺ chelate was effective for conduction; the other silver salts were not suitable to prepare metallized film by heat treatment.

X-ray Analysis

To identify whether the surface of the glass side [or the poly(methyl methacrylate) side] and the air side of the films were metallized or not, the polymer metal chelate films after heat treatment were examined by X-ray diffraction. From the results of X-ray diffraction analysis, as shown in Tables IV–VI, the metallized film clearly demonstrates that the main product on the air side of the film surface was metallic silver for the PVA–AgNO₂, PAN–AgNO₂, and PAN–AgNO₃ chelate solutions by heat treatment. But the X-ray analysis shows that the glass side or poly(methyl methacrylate) side of PVA/AgNO₂, PAN/AgNO₂, and PAN/AgNO₃ film surfaces were nonmetallic, meaning that no reduction occurred during the heat treatment.

CONCLUSION

In this study, excellent electrically conducting metallized polymer films were prepared from PVA–AgNO₂, PAN–AgNO₂, and PAN–AgNO₃ chelate solutions by heat treatment. The process is relatively simple and fast, because the polymer metal chelate solution was dried and reduced to metallized film in one step.

Furthermore, no reducing agents were used, only heat treatment. However, only the PVA–AgNO₂, PAN–AgNO₂, and PAN–AgNO₃ chelates were effective for conduction.

The way in which the different anions in the silver salts, such as silver sulfate, silver acetate, and silver perchlorate, affected the conductivity was investigated under the same conditions as described in the experimental section; favorable results were not obtained. The surface resistivities of PVA or PAN films were more than $2 \times 10^7 \ \Omega/cm^2$.

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