Studies on the Preparation and Properties of Conductive Polymers. IX. Using Photographic Developer to Prepare Metallized Conductive Polymer Films

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SYNOPSIS

Poly(vinyl alcohol) metal chelate solutions were prepared by mixing silver nitrate with solutions of poly(vinyl alcohol), and films were prepared from these solutions. These poly(vinyl alcohol) metal chelate films were reduced by photographic developer. The silver ions in poly(vinyl alcohol) films were reduced to silver on the surface, and conductive polymer films were obtained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Black and white photographic film is composed of very small crystals of a silver halide (usually silver bromide) suspended in a gel: a photographic emulsion coated on a cellulose acetate plastic. When the film is briefly exposed to light, a very small fraction of silver ions in some of the silver halide crystals undergo photochemical decomposition, producing silver atoms. This process is called photosensitization.[1] The process of reducing the sensitized crystals is known as developing, and the reducing agent is the developer.[1]

Volynskii et al.[2] reported that when poly(ethylene terephthalate) film having crazes and pores was placed into a dialysis apparatus AgCl crystals formed in the crazes. Subsequent treatment of the films with a photodeveloper gave highly disperse composites of poly(ethylene terephthalate) with metallic Ag.

In this research, the poly(vinyl alcohol) (PVA) silver chelate solutions were prepared by silver nitrate mixed with PVA and films were prepared from these solutions. These PVA metal chelate films were reduced by a photographic developer. The silver ions in the PVA/AgNO$_3$ chelate films were reduced to silver on the surface of the films, and therefore, metallized conductive polymer films were obtained.

EXPERIMENTAL

Preparation of PVA Silver Chelate Film

Listed in Tables I–V are the conditions of the mixtures with AgNO$_3$ directly added to 10% (by weight) PVA aqueous solution and stirred at room temperature for 24 h. The resulting viscous solution was cast on a poly(methyl methacrylate) plate and first dried under an air atmosphere at ambient for 3 days, and then further dried in an oven at 80°C for one h. The film peeled from the plate is the PVA silver chelate.

Preparation of Metallized Films by Photographic Developer

Test pieces of PVA silver chelate films were reduced at room temperature for a suitable time by photographic developers made up of ferrous sulfate, pyrogallol, hydroquinone, p-phenylenediamine, and p-aminophenol aqueous solution. The reduced films were then washed with water and dried at 100°C for 5 min.

Electric Measurement

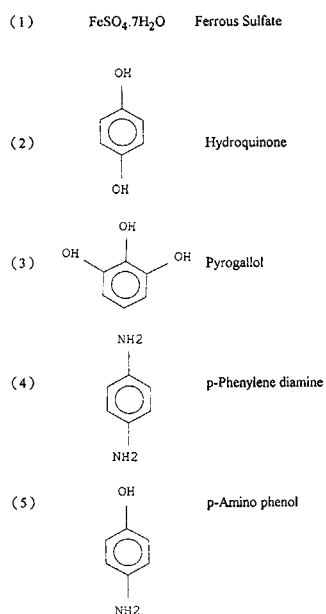Measurement of the surface electrical conductivity of the reduced films was carried out by the conven-

tional four-terminal method with aluminum foil electrodes, as described in a previous article.[3]

X-ray Analysis

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

RESULTS AND DISCUSSION

The following developers[4-7] were used in the study for the preparation of metallized conductive polymer films:

(1) $FeSO_4 \cdot 7H_2O$ Ferrous Sulfate

(2)   Hydroquinone

(3)   Pyrogallol

(4)   p-Phenylene diamine

(5)   p-Amino phenol

The chemical reactions of the development of metal-containing developers are rather simple, and the oxidation of metal ions releases one or more electrons to the silver ions for their reduction to atoms. Most important among such types of developers are solutions containing ferrous salts. In this research, ferrous sulfate aqueous solution is the reducing agent and $PVA/AgNO_3$ chelate film possesses a definite silvery metallic appearance. As shown in Tables I and II, the film surface resistivity decreases with increasing concentration of the ferrous sulfate aqueous solution up to 4.0 wt % and with an increasing amount of silver nitrate in the $PVA/AgNO_3$ chelate films. Within 25.0–30.0 phr of $AgNO_3$ in the PVA chelate films, the films treated by ferrous sulfate aqueous solution exhibit a limiting value of about 10^0–10^{-1} Ω/cm^2. Addition of silver

Table I   Effect of the Concentration and Reduction Time of $FeSO_4$ Aqueous Solution on the Surface Resistivity of $PVA/AgNO_3$ Chelate Films[a]

| Wt %[b]	Time	Surface Resistivity (Ω/cm^2)
1%	20 s	$> 2 \times 10^7$
1%	40 s	1.13×10^5
1%	1 min	7.60×10^4
1%	3 min	3.20×10^4
1%	5 min	2.25×10^4
2%	20 s	4.18×10^4
2%	40 s	6.12×10^4
2%	1 min	4.07×10^3
2%	3 min	1.19×10^2
2%	5 min	5.28×10^1
3%	20 s	1.48×10^2
3%	40 s	4.0×10^0
3%	1 min	4.7×10^0
3%	3 min	5.0×10^0
3%	5 min	2.3×10^0
4%	20 s	2.7×10^0
4%	40 s	5.7×10^0
4%	1 min	1.9×10^0
4%	3 min	1.7×10^0
4%	5 min	1.2×10^1

[a] phr (parts per hundred resin) of $AgNO_3/PVA$ films = 25.0.
[b] The concentration of $FeSO_4$ aqueous solution.

nitrate does not improve the conductivity and gives an unsatisfactory effect such as the loss of flexibility of the metallized conductive polymer films.

Most photographic developers contain electron release groups, among which —OH and —NH_2 are two examples.[8] Common developers consist of 1,4-dihydroxybenzene (hydroquinone) containing two —OH groups, and quinone, a ketone with two carbonyl groups, is the oxidation product as indicated in the reaction below[1,9]:
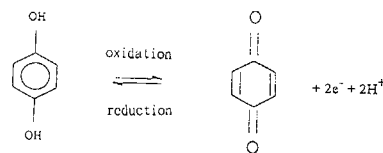
Therefore, conversion of silver ions to metallic silver is effected by these reducing developers:

$$Ag^+ + e^- \rightarrow Ag$$
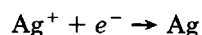
As shown in Table III, an excellent surface resistivity of 10^0–10^1 Ω/cm^2 is obtained for the $PVA/AgNO_3$ chelate films reduced by the pyrogallol

Table II   Effect of the Concentration of AgNO$_3$ on the Surface Resistivity of PVA/AgNO$_3$ Chelate Films Reduced by FeSO$_4$ Aqueous Solution[a]

phr of AgNO$_3$/ PVA Films[b]	Surface Resistivity (Ω/cm^2)
5.0	1.8×10^3
10.0	1.1×10^1
15.0	2.1×10^0
20.0	1.5×10^0
25.0	1.6×10^0
30.0	8.0×10^{-1}

[a] FeSO$_4$ solution: 3 wt %; reduction time: 3 min.
[b] phr = parts per hundred resin.

aqueous solution. When the concentration of pyrogallol aqueous solution was higher than 1 wt %, the surface resistivity of reduced films showed only a little change and exhibited a limiting value of about 10^0 Ω/cm^2.

Shown in Table IV are somewhat higher surface resistivities, around 10^2–10^3 Ω/cm^2 for the 25.0 phr of AgNO$_3$ in the PVA/AgNO$_3$ chelate films treated with p-phenylenediamine aqueous solution, while resistivity is low around 10^1 Ω/cm^2 for the 30.0 phr. Meanwhile, Table IV shows a rising tendency of the film surface resistivity for both 25.0 and 30.0 phr. A film swelling phenomenon is evident for long reduction periods (5 min). The distance between silver particles, originally grown contiguously at the proper reduction time, enlarges to swell the film with the increasing reduction period and raises the film surface resistivity. A p-aminophenol aqueous solution,

Table III   Effect of the Concentration and Reduction Time of Pyrogallol Aqueous Solution on the Surface Resistivity of PVA/AgNO$_3$ Chelate Films[a]

Wt %[b]	Time	Surface Resistivity (Ω/cm^2)
1%	40 s	1.35×10^1
1%	1 min	2.36×10^1
1%	3 min	1.30×10^1
2%	40 s	6.1×10^0
2%	1 min	4.0×10^0
2%	3 min	4.8×10^0
3%	40 s	3.8×10^0
3%	1 min	5.6×10^0
3%	3 min	4.5×10^0

[a] phr (part per hundred resin) of AgNO$_3$/PVA films = 10.0.
[b] The concentration of pyrogallol aqueous solution.

Table IV   Effect of the Reduction Time of p-Phenylenediamine Aqueous Solution[a] on the Surface Resistivity of PVA/AgNO$_3$ Chelate Films

phr of AgNO$_3$/PVA Films[b]	Time	Surface Resistivity (Ω/cm^2)
25.0	40 s	1.1×10^3
25.0	1 min	8.2×10^2
25.0	3 min	7.1×10^2
25.0	5 min	1.5×10^3
30.0	40 s	1.2×10^3
30.0	1 min	3.1×10^1
30.0	3 min	4.6×10^1
30.0	5 min	9.6×10^1

[a] p-Phenylenediamine solution: 1 wt %.
[b] phr = parts per hundred resin.

at a low concentration due to its small solubility in water, is used to reduce the PVA/AgNO$_3$ film. Shown in Table V is a slight increase of the surface resistivity, 10^3–10^4 Ω/cm^2, of the 30.0 phr film reduced by the solution. The decreased reduction ability of the low concentration of the reduction solution accounts for the high surface resistivity of the reduced film.

Kubat et al.[10] reported that a resistivity as low as 0.01 $\Omega \cdot$cm^{-1} can be achieved by simple compounding of fine silver particles with polymeric materials. This method can achieve good conductivity, but the conductivity of pure silver metal represented a four orders of magnitude enhancement compared with this method.

In this research, aluminum foil was used as the electrodes, so the minimum surface resistivity that can be measured is about 4×10^{-1} Ω/cm^2. The reduced films of this work exhibited low surface resistivity around 10^0–10^1 Ω/cm^2, conductivity close to the minimum value. In this research, this method

Table V   Effect of the Reduction Time of p-Aminophenol Aqueous Solution[a] on the Surface Resistivity of PVA/AgNO$_3$ Chelate Films[b]

Time	Surface Resistivity (Ω/cm^2)
40 s	2.5×10^4
1 min	2.3×10^4
3 min	2.2×10^4
5 min	6.3×10^3

[a] p-Aminophenol aqueous solution: 0.4 wt %.
[b] phr (parts per hundred resin) of AgNO$_3$/PVA films = 30.0.

Table VI   Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for PVA/AgNO₃ Chelate Film Reduced by FeSO₄ Aqueous Solution

Film A Experiment[a]		Pure Ag Reference	
2θ	d	2θ	d
38.2	2.354	38.14	2.359
44.4	2.039	44.33	2.034
64.6	1.442	64.50	1.445
77.6	1.229	77.61	1.230

[a] Film A prepared from PVA/AgNO₃ chelate film reduced by FeSO₄ aqueous solution.

is relatively fast and simple and provides excellent metal-like conductivity, so it should be better than conventional compounding.

X-RAY ANALYSIS

The following equation[4] proposes a way for the reduction of PVA/AgNO₃ chelate films by ferrous sulfate aqueous solution to change the film surface:

$$6FeSO_4 + 6AgNO_3 \rightarrow 2Fe_2(SO_4)_3$$
$$+ 2Fe(NO_3)_3 + 6Ag$$
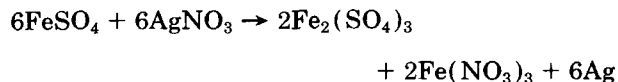
Films were examined using X-ray diffraction to confirm the film surface change mentioned in the equation above and the analysis results clearly demonstrate in Table VI that the main product on the film surface is metallic silver of PVA/AgNO₃ che-

late. Similarly, the PVA/AgNO₃ film surface is reduced to metallic silver when reduced by other photographic developers, such as aqueous hydroquinone solution.

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