

Studies on the Preparation and Properties of Conductive Polymers. X. Using Metal Plates to Prepare Metallized Conductive Polymer Films

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SYNOPSIS

In this article, polymer metal chelate solutions were prepared by metal salts mixed with the polymers containing functional groups such as poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), and polyurethane (PU). These polymer metal chelate solutions were cast on to metal plates, whose oxidation potentials were greater than those of the metal of polymer metal chelate solutions. After heat treatment, the metal ions in the polymer films were reduced to metal on the surface, therefore metallized conductive polymer films were obtained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the previous articles of this series,¹⁻³ metallized polymer films were prepared from polymer metal chelate films. 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 another article of this series,⁴ instead of reducing agents used in the previous work, the effect of heat treatment was investigated. PVA and PAN metal chelate solutions were reduced to metallized polymer films only by heat treatment without reducing agents. These metallized polymers films exhibited low surface resistivity and long-term stability.

When polymer metal chelate film cannot be metallized by a one-step process, such as reduction by reducing agents, the two-stage method to prepare metallized polymer films was utilized. In the

first stage, polymer silver chelate was treated with doping agents. In the second stage, these treated films were further treated with reducing agents or Hg metal. After the two-stage treatment, metallic Ag or Ag-Hg alloy was adhered firmly on the PVA or PAN film surfaces and exhibited excellent conductivity and long-term stability. These experimental method and results were reported in previous articles.^{5,6}

A novel reduction method, retroplating out, for preparing metallized film was also reported in a paper of this series.⁷ Polymer metal chelate films were reduced by wetted metal plates (or metal powders) whose ionization tendencies were greater than that of the metal of these polymer metal chelate films. These reduced films showed excellent conductivity and long-term stability. Owing to the poor contact between the polymer metal chelate films and the metal plate or metal powders, when the films were spread over the wetted metal plate surface or metal powders, the reduced metal would sometimes be distributed over the surface of the polymer metal chelate films in "island" features. In this study, in order to overcome that defect, polymer metal chelate solutions were directly cast on the metal plates. After heat treatment, metallized conductive polymer films were obtained.

Table I Effect of the Amount of Silver Nitrate in PVA Metal Chelate on the Surface Resistivity of Metallized Films^a

AgNO ₃ /PVA (phr) ^b	Surface Resistivity (Ω/cm ²)
5.0	1.088 × 10 ²
10.0	2.466 × 10 ¹
15.0	2.368 × 10 ¹
20.0	1.676 × 10 ¹

^a PVA/AgNO₃ chelate solution reduced by copper plate at 60–70°C for 25 min.

^b phr = parts per hundred resin.

EXPERIMENTAL

Preparation of Polymer Metal Chelate Solutions

PVA, a PAN, and PU metal chelate solutions were prepared by the method that was reported in the previous papers of this series.^{1,4,7}

Reduction of Polymer Metal Chelate Solution by Using Metal Plates

Iron plates and copper plates were used in this reaction. These plates were activated by polishing with emery cloth. These polymer metal chelate solutions were cast on the metal plates, then these plates were placed in a static air oven at 60–70°C for 25 min. The films were peeled from the metal plates, and then cut into 1 cm × 3-cm pieces for electric measurement.

Electric Measurement

The surface electrical conductivity of the films was measured according to the conventional four-terminal method using aluminum foil electrodes, as described in a previous article.⁸

X-Ray Analysis

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

RESULTS AND DISCUSSION

In this study, polymer metal chelate solutions were reduced by metal plates in order to obtain excellent

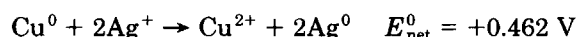
Table II Effect of the Amount of Copper (II) Salt in PVA Metal Chelate on the Surface Resistivity of Metallized Films^a

Solutions	phr ^b	Surface Resistivity (Ω/cm ²)
CuSO ₄ /PVA	5.0	8.020 × 10 ⁰
CuSO ₄ /PVA	10.0	1.548 × 10 ¹
CuSO ₄ /PVA	15.0	6.040 × 10 ⁰
CuSO ₄ /PVA	20.0	1.040 × 10 ⁰
CuCl ₂ /PVA	5.0	2.840 × 10 ¹
CuCl ₂ /PVA	10.0	2.620 × 10 ¹
CuCl ₂ /PVA	15.0	2.330 × 10 ¹
CuCl ₂ /PVA	20.0	1.800 × 10 ¹

^a PVA/copper(II) salt solution reduced by iron plate at 60–70°C for 25 min.

^b phr = parts per hundred resin.

conductive polymer films. As shown in Tables I through III, PVA metal chelate solutions were reduced by metal plates, whose ionization tendencies were greater than those of the metal of the polymer metal chelate solution. These reduced films exhibited definite metallic luster and excellent conductivity (surface resistivity around 10⁰ ~ 10¹ Ω/cm²). The above reaction can take place spontaneously due to the positive net electromotive force value (E_{net}^0). For example, for PVA/AgNO₃ chelate solution after Cu plate treatment, the reaction can be written as follows:



Similarly, the reaction of PVA/CuCl₂ chelate solution after Fe plate treatment can be written as follows:

Table III Effect of the Amount of Copper (II) Nitrate in PVA Metal Chelate on the Surface Resistivity of Metallized Films^a

Cu(NO ₃) ₂ /PVA (phr) ^b	Surface Resistivity (Ω/cm ²)
5.0	> 2 × 10 ⁷
10.0	> 2 × 10 ⁷
15.0	7.570 × 10 ⁰
20.0	4.045 × 10 ⁰

^a PVA/Cu(NO₃)₂ chelate solution reduced by iron plate at 60–70°C for 25 min.

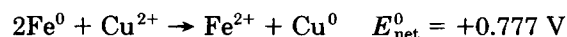
^b phr = parts per hundred resin.

Table IV Effect of the Amount of Silver Nitrate in Polymer Metal Chelate on the Surface Resistivity of Metallized Films^a

Solutions	phr ^b	Surface Resistivity (Ω/cm^2)
AgNO ₃ /PAN	5.0	2.216×10^1
AgNO ₃ /PAN	10.0	1.018×10^1
AgNO ₃ /PAN	15.0	4.020×10^0
AgNO ₃ /PAN	20.0	3.600×10^0
AgNO ₃ /PU	5.0	$> 2 \times 10^7$
AgNO ₃ /PU	10.0	$> 2 \times 10^7$
AgNO ₃ /PU	15.0	4.176×10^1
AgNO ₃ /PU	20.0	2.144×10^1
AgNO ₃ /PU	25.0	3.220×10^0
AgNO ₃ /PU	40.0	9.080×10^0

^a Polymer/AgNO₃ chelate solution reduced by copper plate at 60–70°C for 25 min.

^b phr = parts per hundred resin.



When the E_{net}^0 values were positive, the reaction took place spontaneously. When the E_{net}^0 values were negative, the reduction cannot occur spontaneously.

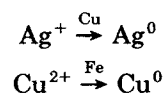
In Tables I and II, for the 5.0 parts per hundred resin (phr) and for more than 5.0 phr of metal salts in the PVA metal chelate treated with the metal plates, the reduced film shows low surface resistivity. In Table II, addition of CuSO₄ did not improve the conductivity and gave unsatisfactory effects such as loss of flexibility of the metallized film. As shown in Table III, when the concentration of Cu(NO₃)₂ is less than 15.0 phr, such as 5.0 and 10.0 phr, the PVA/Cu(NO₃)₂ chelate solutions show unsatisfactory conductivity after Fe plate treatment. Similarly, as shown in Table IV, for PAN/AgNO₃ and PU/AgNO₃ chelate solutions, after Cu plate treatment the film exhibited excellent conductivity.

For the polymer silver nitrate solution after Cu plate treatment, the metallic silver layer firmly adhered to the film and showed excellent stability in air for over 1 year. For PVA-Cu²⁺ chelate solution after Fe plate treatment, the metallic Cu layer on the film surface is unstable in air and the surface resistivity of metallized films show drastic changes with time. ($> 2 \times 10^7 \Omega/\text{cm}^2$)

X-ray Analysis

The polymer metal chelate solutions were treated with metal plates. The change of the surface sub-

stance on the films can be reflected by the following equations:



In order to confirm that the change of surface substance on the film conforms with the above equations, these films were examined by means of X-ray diffraction.

From the result of X-ray diffraction analyses, shown in Table V, the metallized film clearly demonstrates that the main products on the film surface were metallic silver for PVA/AgNO₃ chelate solution reduced by the copper plate and were metallic copper for PVA/CuSO₄ chelate solution reduced by the iron plate. The formation of these metallic silver and copper surface layers were responsible for the conductivity.

CONCLUSION

In this research, polymer metal chelate solutions were prepared by the transition-metal salts mixed with the polymer solution. These polymer metal chelate solutions were cast on metal plates and dried to metallized films. In these reaction, metal ions were reduced to metal and adhered firmly on the surface of polymer film. This method is relatively fast and

Table V Diffraction Angles (2 θ) and Plane Distances (d) Corresponding to Peaks Observed in X-Ray Analysis for Polymer Metal Chelate Solution Reduced by Metal Plate

PVA/AgNO ₃ /Cu Plate Film		Pure Ag Reference	
2 θ	d	2 θ	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
PVA/CuSO ₄ /Fe Plate Film		Pure Cu Reference	
43.3	2.088	43.30	2.088
50.2	1.816	50.43	1.808
74.2	1.277	74.13	1.278

$$\text{Cu}K_{\alpha} = 1.54051 \text{ \AA}$$

simple and obtained excellent metal-like conductivity.

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