Studies on the Preparation and Properties of Conductive Polymers. XI. Metallized Polymer Films by Plating Out

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ABSTRACT: Metallized films were prepared from the plating-out method. Various metal powders with lower reduction potential were dispersed in poly(vinyl alcohol) (PVA) aqueous solution dried to form a film, then treated with metal salt solutions having metal ions in the metal salt with higher reduction potential. Metallized PVA films exhibited low surface resistivity around 10^0–10^1 Ω/cm^2 when using the plating-out method. The surfaces of these films were shown to be metallized by means of X-ray analysis. Scanning electron microscopy (SEM) was also studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1361–1365, 1999

INTRODUCTION

When a piece of zinc is put into an aqueous solution containing Cu^{2+} ions, some of the zinc will be converted to Zn^{2+} ions and dissolved in the water, and the Cu^{2+} ions will be reduced to metallic copper on the surface of the zinc. This reaction can take place spontaneously due to the positive net electromotive force value (E^o_{net}).[1] For example

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad E^o_{net} = +1.100 \text{ V}$$

This reaction is called plating out.[2]

In this study metallized films were prepared from the plating-out method. Various metal powders were dispersed in poly(vinyl alcohol) (PVA) aqueous solution and dried to film, then treated with metal salt solution. In the plating-out reaction, metal ions of metal salts were reduced to metal on the surface of PVA films due to the positive net electromotive force value ($E^o_{net} > 0$).

In the previous article of this series,[3] a novel reduction method for preparing metallized films, retroplating out, was reported. 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. In the plating-out reaction, Cu^{2+} ions are reduced to metallic copper on the surface of a zinc bar. On the contrary, in the novel reaction, Cu^{2+} is reduced to metallic copper and adheres firmly to the surface of polymer film; therefore, the novel reaction is named as retroplating out. These reduced films show excellent conductivity and long-term stability.

EXPERIMENTAL

Preparation of PVA Films

Four g PVA was added to 40.0 ml water and the solution was heated until PVA dissolved completely. Various metal powders (60–120 μm) were added directly to the PVA water solution; these given conditions are listed on Tables I–III. Solutions of these mixtures were stirred vigorously at room temperature and poured into a 15 cm diameter PMMA Petri dish. After 24 h, these Petri dishes were placed in a static oven at 50°C for 12 h. The films were peeled from the Petri dish, and then cut into 1 cm × 3 cm pieces.

Preparation of Metallized Films

The test pieces of PVA film containing metal powders were reduced by metal solutions at room

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Table I Effect of the Amount of Cu Powders on the Conductivity of Cu/PVA Films Reduced by $AgNO_3$ Aqueous Solutions[a]

Cu/PVA (phr)[b]	Reduction Time (s)	Surface Resistivity (Ω/cm^2)
15.0	30	1.8×10^1
20.0	30	3.2×10^1
30.0	30	4.2×10^0
40.0	30	5.3×10^0
50.0	30	6.0×10^0

[a] Concentration of $AgNO_3$ aqueous solutions = 5 wt %.
[b] phr = parts per hundred resin.

Table II Effect of the Amount of Pb Powders on the Conductivity of Pb/PVA Films Reduced by $AgNO_3$ Aqueous Solutions[a]

Pb/PVA (phr)[b]	Reduction Time (s)	Surface Resistivity (Ω/cm^2)
20.0	300	5.8×10^2
30.0	300	1.4×10^2
40.0	300	3.9×10^1
50.0	300	1.8×10^1

[a] Concentration of $AgNO_3$ aqueous solutions = 5 wt %.
[b] phr = parts per hundred resin.

temperature for 10–300 s. The reduced films were washed with water and dried at 100°C for 15 min.

Electric Measurement

The surface electrical conductivity of the reduced film was measured according to the conventional four-terminal method with aluminum foil electrodes, as described in a previous article.[4]

Table III Effect of the Amount of Pb Powders on the Conductivity of Pb/PVA Films Reduced by $CuCl_2$ Aqueous Solutions[a]

Pb/PVA (phr)[b]	Reduction Time (s)	Surface Resistivity (Ω/cm^2)
20.0	300	2.7×10^5
30.0	300	8.0×10^1
40.0	300	5.9×10^1
50.0	300	4.1×10^1

[a] Concentration of $CuCl_2$ aqueous solutions = 5 wt %.
[b] phr = parts per hundred resin.

Table IV Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Cu Powders Dispersed in PVA Film and the Film Reduced by $AgNO_3$ Aqueous Solutions

Cu/PVA Film		Pure Cu Reference	
2θ	d	2θ	d
43.30	2.088	43.30	2.088
50.46	1.807	50.43	1.808
74.16	1.277	74.13	1.278
Cu/PVA/$AgNO_3$ Film		**Pure Ag Reference**	
38.26	2.351	38.14	2.359
44.46	2.036	44.33	2.034
64.62	1.441	64.50	1.445
77.56	1.230	77.61	1.230

CuK_α = 1.54051 Å.

RESULTS AND DISCUSSION

Effect of Various Metal Salt Solutions and Net Electromotive Force Values on the Surface Resistivity of Various Polymer/Metal Powders Films

In this study, metal powders were dispersed in polymer films, and the films were treated by various metal salts solutions in order to obtain excellent conductive polymer films. This method to prepare metallized film was derived from the well-known plating-out method. Metal powders

Table V Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Pb Powders Dispersed in PVA Film Treated with $AgNO_3$ or $CuCl_2$ Solutions

Pb/PVA/$AgNO_3$ Film		Pure Ag Reference	
2θ	d	2θ	d
38.38	2.343	38.14	2.359
44.56	2.032	44.33	2.034
64.72	1.439	64.50	1.445
77.66	1.229	77.61	1.230
Pb/PVA/$CuCl_2$ Film		**Pure Cu Reference**	
43.36	2.085	44.30	2.088
50.54	1.804	50.43	1.808
74.28	1.276	74.13	1.278

CuK_α = 1.54051 Å.

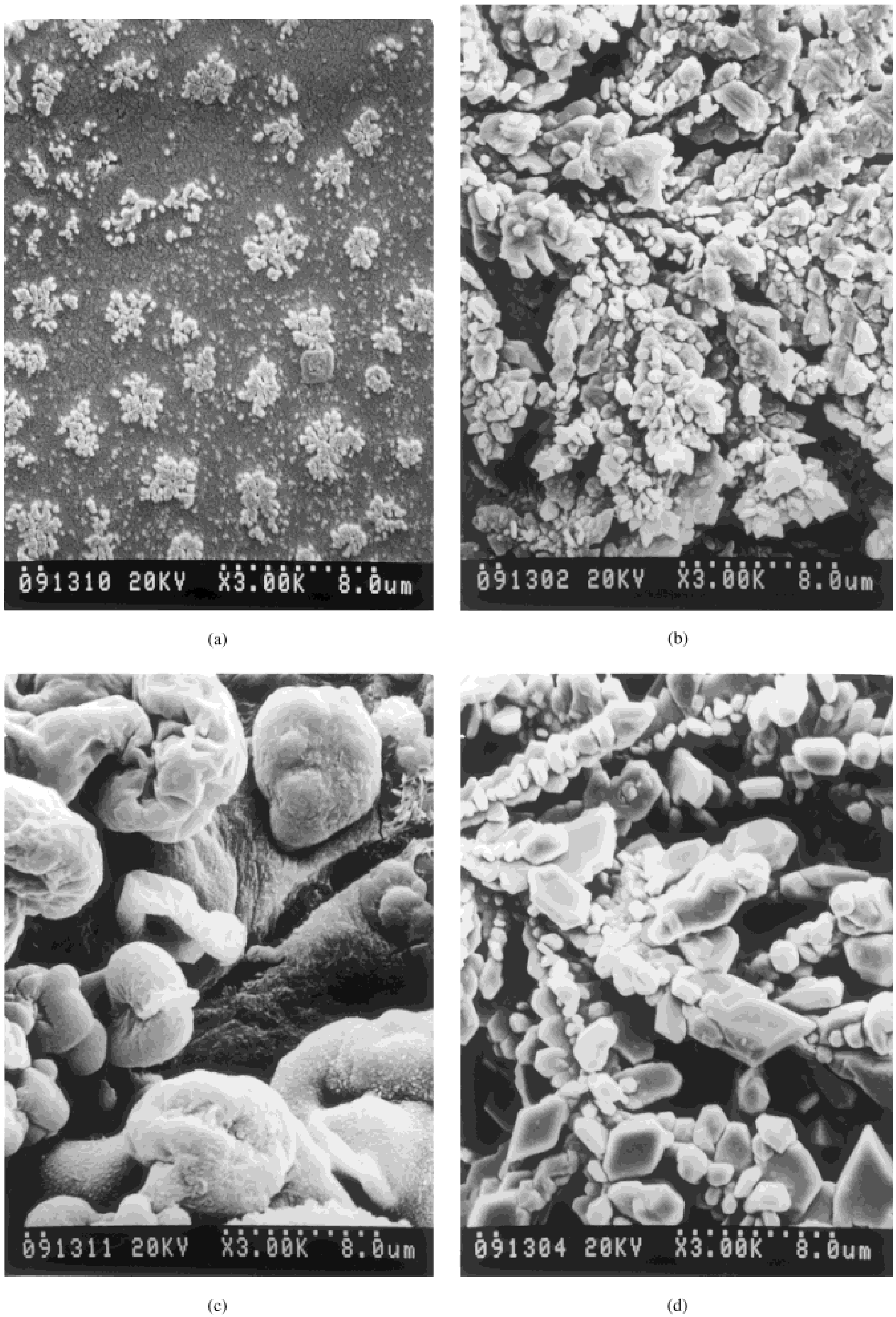
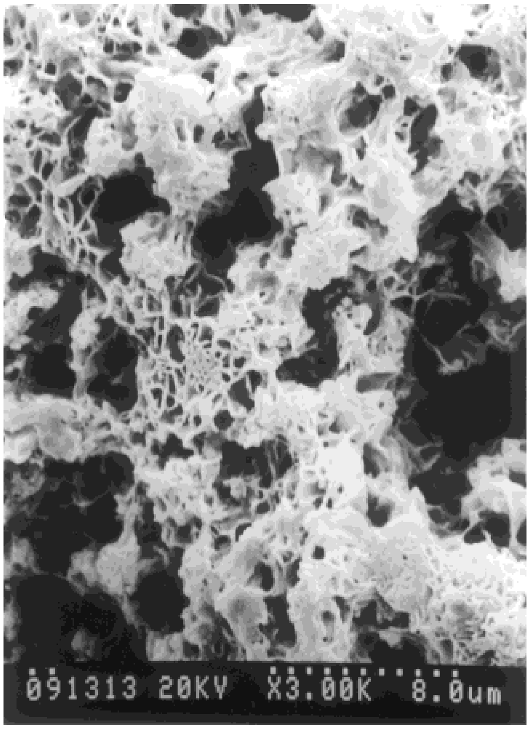

091310 20KV X3.00K 8.0um
(a)
091302 20KV X3.00K 8.0um
(b)
091311 20KV X3.00K 8.0um
(c)
091304 20KV X3.00K 8.0um
(d)

Figure 1.



(e)

Figure 1 (*Continued from previous page*) Scanning electron microscope photographs of the PVA/metal powder films and the films treated with metal solutions. (a) PVA/Cu film (PMMA side). (b) PVA/Cu film treated with $AgNO_3$ solution. (c) PVA/Pb film (PMMA side). (d) PVA/Pb film treated with $AgNO_3$ solution. (e) PVA/Pb film treated with $CuCl_2$ solution.

with lower reduction potential were dispersed in poly(vinyl alcohol) aqueous solution. These solutions were dried to films and treated by metal salts with higher reduction potential. The metal ions of metal salts were reduced to metal and adhered to the surface of polymer film. This oxidation–reduction reaction can take place spontaneously due to the positive net electromotive force value (E^o_{net}). For example, for Cu powders dispersed in PVA film after $AgNO_3$ solution treatment, the reaction can be written as follows

$$Cu^0 + 2Ag^+ \rightarrow Cu^{2+} + 2Ag^0 \quad E^o_{net} = +0.462 \text{ V}$$

Similarly, the reaction of Pb powders dispersed in PVA films after $AgNO_3$ solution treatment and Pb powders dispersed in PVA film after $CuCl_2$ solution treatment can be written as follows

$$Pb^0 + 2Ag^+ \rightarrow Pb^{2+} + 2Ag^0 \quad E^o_{net} = +0.925 \text{ V}$$

$$Pb^0 + Cu^{2+} \rightarrow Pb^{2+} + Cu^0 \quad E^o_{net} = +0.463 \text{ V}$$

As shown in Tables I through III, these metal powders dispersed in PVA film exhibited low surface resistivity around 10^0–10^2 Ω/cm^2 when reduced by metal solutions.

In Table I, for the 15.0 parts per hundred resin (phr) and for more than 15.0 phr of Cu powders in the PVA film treated with $AgNO_3$ solution, the reduced film shows low surface resistivity. As shown in Tables II and III, when the concentration of Pb powders as less than 30.0 phr, the PVA films show unsatisfactory conductivity after $AgNO_3$ or $CuCl_2$ solution treatment. Since the density of metal powders is greater than the PVA solution, these metal powders sink to the bottom of the PMMA Petri dish while the solutions dry to films; only the PMMA side of the PVA film is reduced to metal after metal solution treatment. There is no change on the air side of the PVA film after metal solution treatment.

For Cu or Pb powders dispersed in PVA film after $AgNO_3$ solution treatment, the metallic Ag layer firmly adhered to the film and showed excellent stability in air for over 1 year. For Pb powders dispersed in PVA film after $CuCl_2$ solution treatment, the metallic Cu layer on the film surface is unstable in air, and after 24 h the film show high surface resistivity ($>2 \times 10^7$ Ω/cm^2).

X-ray Analysis

X-ray diffraction was adopted to examine the substance of the surface of untreated and treated films. From the results of X-ray diffraction analyses, shown in Table IV, the main substance on the PMMA side of the film surface is Cu for Cu powders dispersed in the PVA film, and the main product is metallic Ag for the film treated with $AgNO_3$ solutions. Similarly, as shown in Table V, the main product is metallic Ag or Cu for Pb powders dispersed in PVA film treated with $AgNO_3$ or $CuCl_2$ solutions.

SEM Observations

As shown in Figure 1(a),the PMMA side of the film surface shows "island" features for Cu powders dispersed in PVA film, and in Figure 1(b), these metallic Ag particle aggregates form a continuous distribution on the surface of the film after $AgNO_3$ solution treatment. Since the particle size of Pb powders is smaller than Cu powders, the PMMA side of the film surface shows a continuous distribution for Pb powders dispersed in PVA film, as shown in Figure 1(c). Surfaces of these films, after $AgNO_3$ or $CuCl_2$ solution treatment, exhibited good conductivity because of the aggregation of continuous metallic Ag or Cu, as shown in Figure 1(d) and 1(e).

CONCLUSION

In this research, various metal powders with lower reduction potential were dispersed in PVA films, and reduced by metal salt solutions that metal ions in the metal salt with higher reduction potential. Metal ions were reduced to metal and adhered firmly on the surface of PVA film. This method is relatively fast, simple, and provides excellent metal-like conductivity.

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