

Studies on the Preparation and Properties of Conductive Polymers. III. Metallized Polymer Films by Retroplating Out

CHUEH-JUNG HUANG,¹ CHIH-CHAO YEN,² and TEH-CHOU CHANG^{2,*}

¹Shu-Teh Junior College of Technology, Taichung, Taiwan, Republic of China and ²Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan 32023, Republic of China

SYNOPSIS

A novel method to prepare polymer metallized films was found by using polymer metal chelate films treated with wetted metal plates (or metal powders). The polymer metal chelate films were prepared by metal salts mixed with the polymers containing a functional group, such as poly(vinyl alcohol) (PVA), polyamide, polyacrylamide (PAAm), and polyurethane (PU). This novel method is called the retroplating-out method. Polymer metallized films exhibited low surface resistivity around $10^{-1} \Omega/\text{cm}^2$ by using this novel method. The surfaces of these films were shown to be metallized by means of X-ray analysis. The conduction mechanism was verified reasonably well by using scanning electron microscope (SEM) and UV-visible absorption data.

INTRODUCTION

Much attention has been given to polymer metal chelate films that are formed by polymers containing functional groups with dissolved metal salts that can be chemically modified for the purpose of imparting electrical conductivity.^{1,2}

In the first paper of this series,³ a novel method was described concerning easily processed conductive polymer film prepared from poly(vinyl alcohol) (PVA). PVA metal chelate film exhibits very low surface resistivity around $10^0 \Omega/\text{cm}^2$ when reduced by certain agents, such as aqueous sodium borohydride (NaBH_4), sodium (Na) in ethanol, iron (Fe) powder in dilute acetic acid, or catalytic hydrogenation with palladium/charcoal (or Raney nickel) in ethanol. Similarly, in the second paper of this series,⁴ polyamide metal chelate films were used. When polyamide metal chelate films were reduced by aqueous sodium borohydride, the films obtained showed satisfactory electrical conductivity similar to PVA metal chelate films. After reduction, the surface of these films was proved to be metallized by means of X-ray and ESCA analysis. These metallized films were very stable in air.

A new reduction system to prepare metallized film is reported here. The polymer metal chelate films were prepared by metal salts mixed with the polymers containing functional groups such as PVA, polyamide, polyacrylamide (PAAm), and polyurethane (PU). These polymer metal chelate films were reduced by wetted metal plates or metal powders, whose ionization tendencies were greater than those of the metal of polymer metal chelate films. Excellent conductive films with long-term stability were obtained. In this study, the novel reaction to prepare metallized film is named as retroplating out.

EXPERIMENTAL

Preparation of Polymer Metal Chelate Films

PVA and polyamide metal chelate films were prepared by the method that was reported in the previous papers of this series.^{3,4} Polyacrylamide (PAAm) metal chelate films were prepared by a similar method as for the PVA metal chelate films.³

Two parameters are used to express the amount of metal salts in the polymer metal chelate:

1. $\text{Wt \%} = (\text{metal salt weight/polymer weight}) \times 100\%$.

* To whom correspondence should be addressed.

2. F value = molar concentration of metal salts/
molar concentration of monomeric units of
the polymers.

In this study, commercially available polyurethanes, which were synthesized from toluene diisocyanate (TDI) and polyols, were used. Metal salts dissolved in *N,N*-dimethylformamide (DMF) were mixed with commercially available polyurethane DMF solution to make a viscous polyurethane metal chelate solution. The resulting viscous solution was cast on glass plates and dried at 135°C for 1 h.

Retroplating-out Reaction

The procedures to prepare metallized films by using wetted metal plates or metal powders to reduce polymer metal chelate films are described as the following:

Reduction of PVA and PAAm Metal Chelate Films

Various activated metal plates or commercially available activated metal powders were used in this reaction. The metal plates were activated by polishing with emery cloth. Distilled water was spread on the metal plates or metal powders, then a piece of PVA or PAAm metal chelate film was put onto the surface of the wetted metal plates or metal powders at room temperature for about 5–10 s to induce the retroplating out. The reduced film was washed with water several times and dried at 100°C for 15 min.

Reduction of Polyamide and PU Metal Chelate Films

Polyamide or polyurethane metal chelate films were put onto the surface of wetted metal plates or metal powders that were preheated to 100°C for about 20 s to 5 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 elsewhere.²

UV-Visible Absorption Spectra Analyses

UV-Visible absorption spectral data of PVA–Ag⁺ chelate films were obtained by using Jasco model 7800 spectrophotometer. PVA–Ag⁺ chelate films (0.1 wt %–25 wt %; $F = 0.00026$ – $F = 0.065$) were

prepared by the method that was reported in the first paper of this series.³ These films were controlled to 30 μm in thickness and cut into test pieces of size 1 × 3 cm. These test pieces were dipped into 10 mL water at room temperature for 20 s to 12 h, followed by the AgNO₃ diffusion from the polymeric metal chelate film into the aqueous solution. Absorption spectral data of these aqueous solutions was also obtained by UV-visible spectrophotometry.

SEM Observation

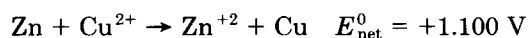
The surfaces of various weight percents of unreduced and reduced polymer metal chelate films, coated with gold film of 150 Å thickness, were measured under a Hitachi model S570 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Effect of Various Wetted Metal Plates (or Metal Powders) and Net Electromotive Force Values on the Surface Resistivity of Various Polymer Metal Chelate Films

In this study, polymer metal chelate films were reduced by various wetted metal plates (or metal powders) in order to obtain excellent conductive polymer films. This novel method to prepare metallized film was derived from the well-known plating-out method.⁵ A piece of zinc is put into an aqueous solution containing Cu²⁺ ions, some of the zinc will be converted to Zn²⁺ ions and dissolved in the water, and the Cu²⁺ ions will be reduced to metallic copper on the surface of zinc.

This reaction can take place spontaneously due to the positive net electromotive force value (E_{net}^0).⁶ For example,



This reaction is called plating out.

Actually, it also means that the polymer metal chelate films can be reduced to metallized films when the metal plates or metal powders show greater ionization tendencies than does the metal of a polymer metal chelate used as reducing agent under the wetted condition. But the phenomenon of this novel reaction is quite different from plating out. In the plating-out reaction, Cu²⁺ ions are reduced to metallic copper on the surface of zinc bar. On the contrary, in this novel reaction, Cu²⁺ is reduced to metallic copper and adhered firmly on the surface of

Table I Effect of Various Wetted Metal Plates (or Powders) and Net Electromotive Force Value on the Surface Resistivity of Various Polymer Metal Chelate Film

| Run | Film | F | Wt % | Metal Plates (or Metal Powders) | E_{net}^0 | Surface Resistivity (Ω/cm^2) |
|-----|---|-------|------|------------------------------------|-------------|--|
| 1 | PVA/AgNO ₃ | 0.039 | 15.0 | Cu | +0.462 | 1.0×10^{-1} |
| 2 | | | | Sn | +0.935 | 1.0×10^{-1} |
| 3 | | | | Fe | +1.239 | 1.0×10^{-1} |
| 4 | PVA/CuCl ₂ · 2H ₂ O | 0.078 | 30.1 | Zn | +1.562 | 1.0×10^{-1} |
| 5 | | | | Al | +2.461 | 1.0×10^{-1} |
| 6 | | | | Sn | +0.473 | 1.0×10^{-1} |
| 7 | | | | Fe | +0.777 | 1.0×10^{-1} |
| 8 | | | | Zn | +1.100 | 1.0×10^{-1} |
| 9 | PVA/NiCl ₂ · 6H ₂ O | 0.075 | 40.5 | Zn | +0.513 | 3.1×10^0 |
| 10 | PVA/CoCl ₂ · 6H ₂ O | 0.075 | 40.5 | Zn | +0.486 | 4.3×10^1 |
| 11 | PVA/NiCl ₂ · 6H ₂ O | 0.075 | 40.5 | Fe | +0.190 | $> 2 \times 10^7$ |
| 12 | PVA/CoCl ₂ · 6H ₂ O | 0.075 | 40.5 | Fe | +0.163 | $> 2 \times 10^7$ |
| 13 | PVA/NiCl ₂ · 6H ₂ O | 0.075 | 40.5 | Sn | -0.114 | $> 2 \times 10^7$ |
| 14 | PVA/CoCl ₂ · 6H ₂ O | 0.075 | 40.5 | Sn | -0.141 | $> 2 \times 10^7$ |
| 15 | PVA/NiCl ₂ · 6H ₂ O | 0.075 | 40.5 | Cu | -0.587 | $> 2 \times 10^7$ |
| 16 | PVA/CoCl ₂ · 6H ₂ O | 0.075 | 40.5 | Cu | -0.614 | $> 2 \times 10^7$ |
| 17 | Nylon 6/CuCl ₂ · 2H ₂ O | 0.150 | 22.6 | Fe | +0.777 | 1.1×10^0 |
| 18 | PAAm/AgNO ₃ | 0.20 | 30.9 | Fe | +0.777 | 0.6×10^0 |
| 19 | | 0.100 | 24.0 | Cu | +0.462 | 6.0×10^0 |
| 20 | | — | — | Fe | +1.239 | 1.0×10^{-1} |
| 21 | PU/AgNO ₃ | — | 25.0 | Cu | +0.462 | 1.0×10^{-1} |
| 22 | | — | 25.0 | Fe | +1.239 | 1.4×10^0 |

polymer film; therefore, we name this novel reaction system as retroplating out.

As shown in Table I (runs 1–10), when the E_{net}^0 values are positive, these PVA metal chelate films exhibited definite metallic luster and excellent conductivity (surface resistivity around $1.0 \times 10^{-1} \Omega/\text{cm}^2$). The minimum value of surface resistivity measured by the four-terminal method is $1.0 \times 10^{-1} \Omega/\text{cm}^2$. As shown in Table I (runs 11 and 12), the films show high surface resistivity ($> 2 \times 10^7 \Omega/\text{cm}^2$) because the reduction cannot take place easily at small positive E_{net}^0 values. The surface conduction of the reduction for the treated films was the same

as that of the untreated ones in appearance. In runs 13–16 in Table I, when the E_{net}^0 values were negative, the reduction cannot occur spontaneously. The films also have high surface resistivity ($> 2 \times 10^7 \Omega/\text{cm}^2$). Again, there were no observed differences between treated and untreated films in appearance.

Similarly, polyamide, PAAm, and PU metal chelate films were reduced by wetted metal plates or metal powders. These films show excellent conductivity due to the higher positive E_{net}^0 values, as shown in Table I (runs 17–22).

In the first paper of this series,³ it was shown that PVA can be coordinated with Ag⁺ or Cu²⁺ ions

Table II Effect of Sodium Borohydride Solution on the Surface Resistivity of PVA Metal Chelate Film

| Film | F | Wt % | Surface Resistivity (Ω/cm^2) |
|---|-------|------|---|
| PVA/AgNO ₃ | 0.039 | 15.0 | 1.0×10^{-1} |
| PVA/CuCl ₂ · 2H ₂ O | 0.078 | 30.1 | 1.0×10^{-1} |
| PVA/NiCl ₂ · 6H ₂ O | 0.075 | 40.5 | 1.0×10^{-1} |
| PVA/CoCl ₂ · 6H ₂ O | 0.075 | 40.5 | 1.0×10^{-1} |
| PVA/FeCl ₃ · 6H ₂ O | 0.150 | 92.2 | 1.0×10^{-1} |

and a PVA metal chelate is formed. The PVA-Ag⁺ and PVA-Cu²⁺ chelate films reduced by NaBH₄ aqueous solution exhibits excellent electrical conductivity. PVA can also be coordinated with Ni²⁺, Co²⁺, and Fe³⁺ ions. These PVA metal chelate films can be reduced by NaBH₄ aqueous solution to exhibit excellent conductivity as well, as shown in Table II. From Table II, it is noted that the minimum amount of CuCl₂, NiCl₂, and CoCl₂ needed in the PVA metal chelate to prepare metallized films was higher than the amount of AgNO₃ required. Furthermore, the minimum amount of FeCl₃ needed in the PVA metal chelate to prepare metallized films was higher than that required of CuCl₂, NiCl₂, and CoCl₂. It is shown that the minimum amount of metal salts needed in the PVA metal chelate increases with the increasing valence of metal salts.

Effects of the Amount of Silver Nitrate in PVA Metal Chelate Films on the Conductivity of Metallized Films

In Table III, for the 5 wt % ($F = 0.013$) and 10 wt % ($F = 0.026$) of AgNO₃ in the PVA-Ag⁺ chelate films treated with the wetted metal plates or metal powders, respectively, the surface resistivities are still greater than $2 \times 10^7 \Omega/\text{cm}^2$. When the amount of silver nitrate in the PVA-Ag⁺ chelate film is more than 10 wt % ($F > 0.026$), the film shows excellent conductivity (surface resistivity around $10^{-1} \Omega/\text{cm}^2$) after being reduced by wetted metal plates or metal powders. These results are similar to those of the PVA-Ag⁺ chelate film reduced by NaBH₄ aqueous solution as mentioned in the first paper of this series.³

X-Ray Analysis

X-ray diffraction is adopted to examine the metallization of the surface of treated films. From the

Table III Effect of the Amount of Silver Nitrate in PVA Metal Chelate Film on the Surface Resistivity of Metallized Films

| F | Wt % | Surface Resistivity (Ω/cm^2) |
|-------|------|--|
| 0.013 | 5.0 | $> 2 \times 10^7$ |
| 0.026 | 10.0 | $> 2 \times 10^7$ |
| 0.039 | 15.0 | 1.0×10^{-1} |
| 0.052 | 20.0 | 1.0×10^{-1} |
| 0.065 | 25.0 | 1.0×10^{-1} |
| 0.078 | 30.0 | 1.0×10^{-1} |

Table IV Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Polymer Chelate Film Reduced with Wetted Metal Plates (or Powders)

| Peaks | Film A ^a Experiment | | Pure Cu Reference | |
|-------|-----------------------------------|-------|----------------------|-------|
| | 2θ | d | 2θ | d |
| 1 | 43.3 | 2.088 | 43.30 | 2.088 |
| 2 | 50.4 | 1.809 | 50.43 | 1.808 |
| 3 | 74.1 | 1.279 | 74.13 | 1.278 |

^a Film A prepared from PVA/CuCl₂ and polyamide/CuCl₂ chelate film reduced by wetted zinc plates (or powders).

results of X-ray diffraction analyses, shown in Table IV, the metallized film clearly demonstrates that the main products on the film surface are metallic copper for PVA/CuCl₂ and polyamide/CuCl₂ films, which are reduced by wetted zinc plates or zinc powders. The results of PVA/AgNO₃, PAAm/AgNO₃, and PU/AgNO₃ films reduced by the wetted metal plates or metal powders show that the surface of these films were reduced to metallic silver, as shown in Table V. The formation of these metallic copper and silver surface layers were responsible for the conductivity.

In retroplating out, it is noted that chelate holds the metallic substance on the surface of film and it acts as an "anchor." Therefore, the metallic substance layer adhered to the film very firmly and was stable for over 1 year.

Visible and UV Spectra Observations

The UV-visible spectrophotometries of various wt % PVA-Ag⁺ films were studied in order to identify

Table V Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for Polymer Chelate Film Reduced with Wetted Metal Plates (or Powders)

| Peaks | Film B ^a Experiment | | Pure Ag Reference | |
|-------|-----------------------------------|-------|----------------------|-------|
| | 2θ | d | 2θ | d |
| 1 | 38.1 | 2.360 | 38.14 | 2.359 |
| 2 | 44.3 | 2.043 | 44.33 | 2.043 |
| 3 | 64.4 | 1.446 | 64.50 | 1.445 |
| 4 | 77.5 | 1.231 | 77.61 | 1.230 |

^a Film B prepared from PVA/AgNO₃, PAAm/AgNO₃, and PU/AgNO₃ chelate film reduced by wetted copper (or powders).

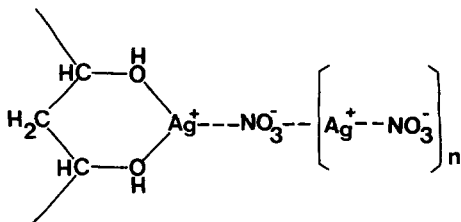


Figure 1 Proposed structure for the PVA- Ag^+ chelate responsible for conductivity.

the proposed structure responsible for the conductivity (Fig. 1).³ As shown in Figure 2, the UV-visible spectral band of the 0.1 wt % ($F = 0.00026$) PVA- Ag^+ film appears at 433 nm and has a dark-brown color, which are two characteristics of chelate formation for Ag^+ coordinated with hydroxy group of PVA. This chelate structure of PVA- Ag^+ was proposed in Figure 3. When the AgNO_3 wt % of the PVA- Ag^+ film is greater than 0.1 wt % ($F > 0.00026$), the UV-visible absorption spectral bands appear at 433 and 208 nm.

The spectral band at 208 nm was attributed to the UV absorption of AgNO_3 aqua complex. It appears that when the amount of AgNO_3 in the PVA- Ag^+ chelate film is greater than 0.1 wt %, some of the Ag^+ ions were first coordinated with the hydroxy group of PVA; then, the surplus Ag^+ ions are not chelated by PVA but coordinated by the NO_3^- ion. Therefore, the absorbance of 433 nm was not in-

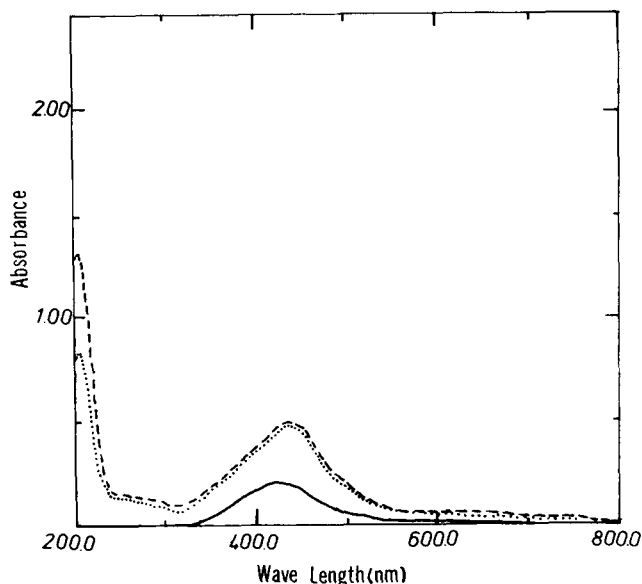


Figure 2 Visible and UV absorption spectra: (a) (—) 0.1 wt % PVA- Ag^+ film; (b) (\cdots) 0.2 wt % PVA- Ag^+ film; (c) (---) 0.5 wt % PVA- Ag^+ film.

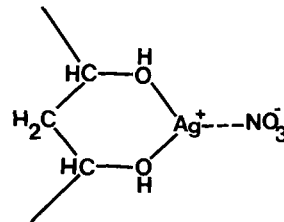


Figure 3 Proposed structure for the PVA- Ag^+ chelate.

creased by increasing the amount of AgNO_3 in the PVA- Ag^+ chelate, but the absorbance of 208 nm was increased by increasing the amount of AgNO_3 in the PVA- Ag^+ chelate.

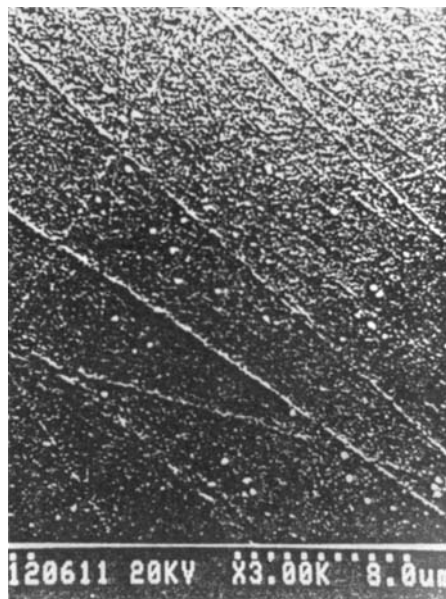
The results are in good agreement with that of the PVA- Ag^+ chelate structure (Fig. 1) provided in the first paper of this series.³ The NO_3^- ion is considered to be the bridging atom to form the activated complex. Therefore, the surplus AgNO_3 in the activated complex can be easily reduced to metallic Ag on the film surface by various reducing agents or the retroplating-out reaction. The metallic Ag was held by the chelate like an "anchor," and the metallic Ag adhered to the film rather firmly; thus, the metallized film was very stable in the air for a long time. Therefore, chelate plays a very important role on the conductivity.

Further research was carried out by dipping the test pieces into water to detect the amount of AgNO_3 diffuse out from the PVA- Ag^+ chelate film by using a UV-visible spectrophotometer. As shown in Table VI, the 0.1 wt % PVA- Ag^+ chelate film was dipped into water over 12 h; the absorbance of AgNO_3 was still zero, this being ascribed to Ag^+ ions with PVA forming strong coordinate covalent bond. When the amount of AgNO_3 was greater than 0.1 wt %, the absorbance of AgNO_3 in the PVA- Ag^+ chelate film dipped into water was increased by increasing the

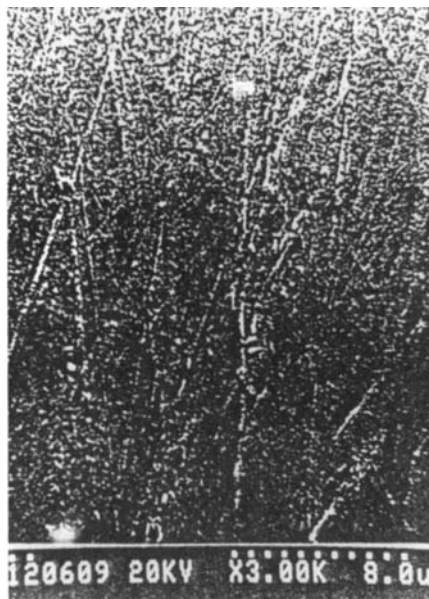
Table VI The Absorbance of PVA- Ag^+ Chelate Film Dipped into Water for 20 s

| F | Wt % | Absorbance |
|---------|------|------------------------------|
| 0.065 | 25.0 | 2.1998 |
| 0.052 | 20.0 | 1.7486 |
| 0.039 | 15.0 | 1.2335 |
| 0.026 | 10.0 | 0.3777 |
| 0.013 | 5.0 | 0.0570 (0.079 ^a) |
| 0.0013 | 0.5 | 0.0000 (0.048 ^a) |
| 0.00026 | 0.1 | 0.0000 (0.000 ^a) |

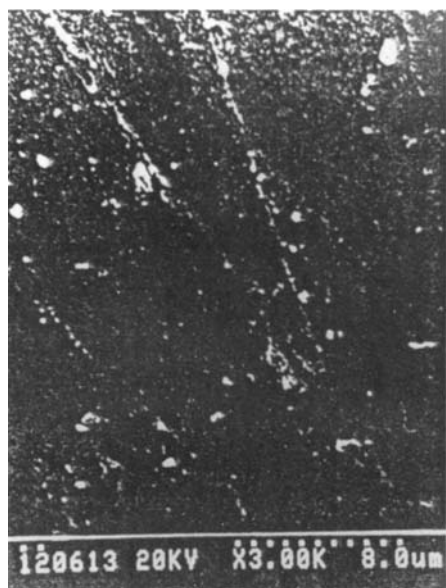
^a Absorbance of PVA- Ag^+ chelate films soaked into water for 12 h.



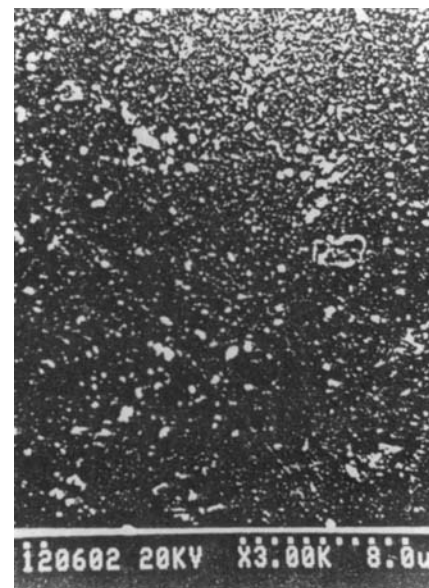
(a) 5 wt% PVA-Ag⁺ film before Cu treatment



(b) 10 wt% PVA-Ag⁺ film before Cu treatment



(c) 5 wt% PVA-Ag⁺ film after Cu treatment



(d) 10 wt% PVA-Ag⁺ film after Cu treatment

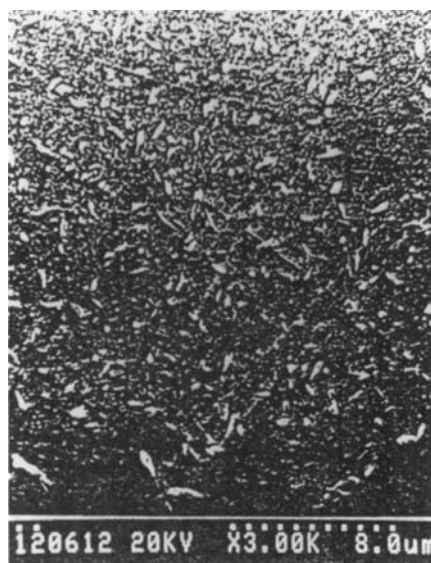
Figure 4 Scanning electron microscope photographs of the PVA-Ag⁺ chelate film before and after wetted metal treatment.

amount of AgNO₃ in the PVA-Ag⁺ chelate film, as shown in Table VI. These results indicated that the surplus AgNO₃ in the PVA-Ag⁺ chelate film can be diffused into aqueous solution and simultaneously be reduced by aqueous solution of reducing agents into a metallic state that adheres to the surface of

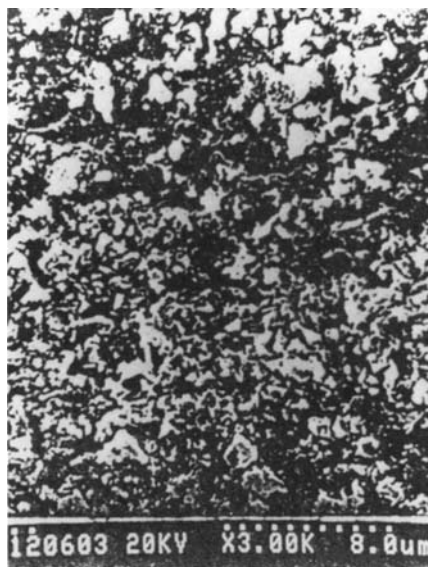
the film. In the 0.1 wt % PVA-Ag⁺ chelate film, no AgNO₃ diffuses into aqueous solution as mentioned above; therefore, it is suggested that the Ag⁺ ion is by itself enough to coordinate with PVA and there are no surplus Ag⁺ ions to form an activated complex in the 0.1 wt % PVA-Ag⁺ chelate film. Besides, the



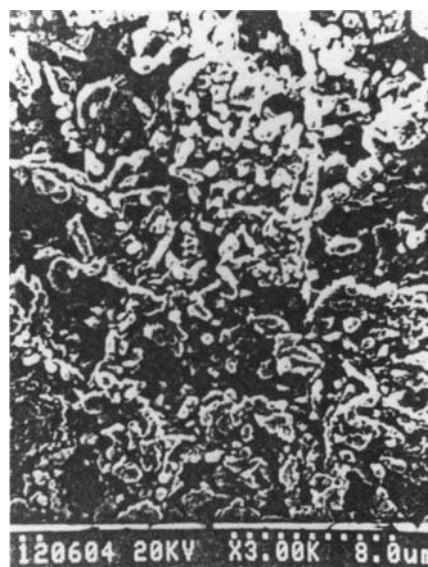
(e) 5 wt% PVA-Ag⁺ film
after Na/C₂H₅OH treatment



(f) 10 wt% PVA-Ag⁺ film
after Na/C₂H₅OH treatment



(g) 15 wt% PVA-Ag⁺ film
after Cu treatment



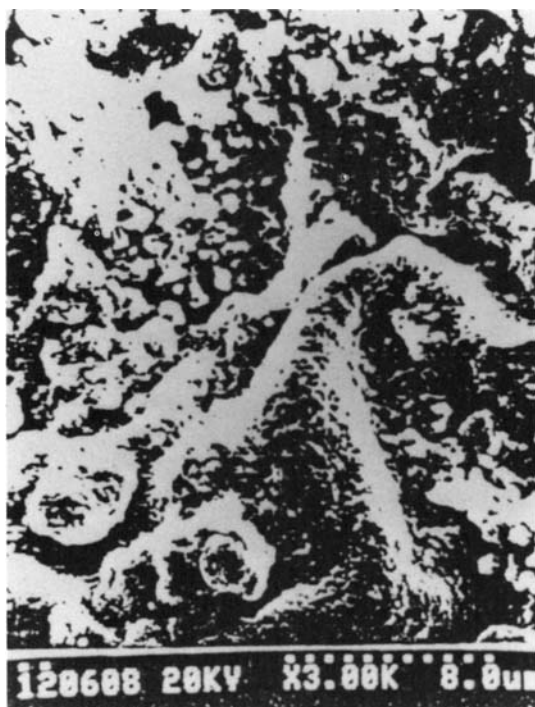
(h) 15 wt% PVA-Ag⁺ film
after Fe treatment

Figure 4 (Continued from the previous page)

color of this film does not fade after dipping it into aqueous solution, which indicates that Ag⁺ ions with PVA formed a strong coordinate covalent bond due to chelate formation. Therefore, the structure of 0.1 wt % PVA-Ag⁺ chelate was in good agreement with Figure 3, as mentioned above.

It should be noted that the solvents of reducing agents played another important role in the conductivity. In the first paper of this series,³ PVA metal

chelate film was reduced by various reducing agents, such as aqueous sodium borohydride (NaBH₄), sodium (Na) in ethanol, iron (Fe) powder in dilute aqueous acetic acid, and catalytic hydrogenation with palladium charcoal (Pd/C) (or Raney nickel) as a catalyst in ethanol solution. Because the metal ions in the PVA metal chelate can easily diffuse into these solvents, it can be reduced to the metallic state by these reducing agents. Therefore, PVA metal



(i) 24 wt% PAAm-Ag⁺ film
after Fe treatment



(j) 25 wt% PU-Ag⁺ film
after Fe treatment

Figure 4 (Continued from the previous page)

chelate film can be converted into metallized film by various reducing agents. In the second paper of this series,⁴ polyamide metal chelate film can be reduced only by aqueous sodium borohydride (NaBH₄). This is ascribed to metal ions in the polyamide metal chelate diffusing only into aqueous solution but not into any other organic solvent, meaning that polyamide metal chelate can be reduced to the metallic state only by aqueous sodium borohydride. In the retroplating out, PVA metal chelate films can be reduced to the metallic state by spreading water, ethanol, and methanol on the metal plates (or metal powders). This is due to the metal ions in the PVA metal chelate films diffusing into water, ethanol, and methanol. When PAAm, polyamide, and PU metal chelate films are reduced by spreading ethanol or methanol on the metal plates (or metal powders) whose ionization tendencies are greater than that of the metal of these polymers, metal chelate films could not be reduced to the metallic state because no metal ions can diffuse into ethanol or methanol from the films. Therefore, it is suggested that only using water as a solvent for the reducing agents can reduce PAAm, polyamide, and PU metal chelate films to metallized films.

SEM Observations

As mentioned above, PVA-Ag⁺ chelate film after being reduced by the wetted metal plates (or metal powders) shows excellent conductivity, because the AgNO₃ wt % of the PVA-Ag⁺ chelate film is equal to or more than 15 wt % ($F \geq 0.039$), but for the films with less than 15 wt % ($F < 0.039$), high surface resistivity is shown. These results can be supported by SEM photographs. The 5 wt % ($F = 0.013$) and 10 wt % ($F = 0.026$) PVA-Ag⁺ chelate films show highly flat surfaces, as shown in Figure 4(a) and (b). When these PVA-Ag⁺ chelate films were reduced by the wetted Cu plates, only some of Ag⁺ ions were reduced to metallic silver. In Figure 4(c) and (d), the metallic silver was distributed over the surface of PVA-Ag⁺ chelate film like "island" features. Therefore, these reduced films show high surface resistivity ($> 2 \times 10^7 \Omega/\text{cm}^2$). The surfaces of 5 wt % ($F = 0.013$) and 10 wt % ($F = 0.026$) PVA-Ag⁺ chelate films that were reduced by sodium in ethanol also show "island" features [Fig. 4(e) and (f)]. The 15 wt % or more ($F \geq 0.039$) PVA-Ag⁺ chelate films were reduced by the wetted Cu or Fe plate (or powders), respectively. These metallic Ag

particle aggregates on the surfaces of the reduced film formed a continuous distribution, shown in Figure 4(g) and (h). Therefore, these reduced films possess excellent conductivity. Similarly, PAAm-Ag⁺ and PU-Ag⁺ chelate films are also reduced by the wetted Fe plate (or powders). The AgNO₃ wt % of the PAAm-Ag⁺ chelate film and PU-Ag⁺ chelate film were 24 and 25, respectively. These films' surfaces exhibited good conductivity because of the aggregation of continuous metallic Ag, as shown in Figure 4(i) and (j).

These results also can be proved by the fact that when the PVA-Ag⁺ chelate film was dipped into water for 20 s, the absorbances of 10 wt % ($F = 0.026$) or less were much less than were the absorbances of 15 wt % ($F = 0.039$) or more, as shown in Table VI. Therefore, only some of Ag⁺ ions in the PVA-Ag⁺ chelate film can diffuse into water. The surface of the PVA-Ag⁺ chelate film showed a high surface resistivity, indicating that only a small amount of metallic Ag was reduced.

CONCLUSION

To obtain excellent electrically conducting metallized polymer films by the retroplating-out method, the following steps should be noted:

1. Adopt polymers containing functional groups such as poly(vinyl alcohol) (PVA), polyamide, polyacrylamide (PAAm), and polyurethane (PU).
2. Introduce enough metal salt solution into the polymer solution to form the polymer metal chelate film.
3. Reduce by wetted metal plates (or metal powders) that have ionization tendencies greater than those of the metal of polymer metal chelate films, and reduce metal ions to metallic states on the surfaces of polymer films.

4. Form metallized polymer films with excellent electrical conductivity.

These processes are very simple and fast, and the conductivity of metallized polymer films were very stable in the air for a long time. Furthermore, these metallized polymer films maintained satisfactory mechanical properties.

This research is being extended by using a series of polyamide-imide metal chelate films prepared by the transition-metal salts (AgNO₃, CuCl₂, CoCl₂, and NiCl₂) mixed with the polyamide-imide solution. These polyamide-imide metal chelate films are reduced by various reducing agents and show excellent conductivities. These precise studies are now in progress and will be reported in the near future.

The authors are indebted to the National Science Council of the Republic of China for financial support of this work by grant NSC-79-0405-E033-02. They are also grateful to Prof. Hsu Keh-Ying and Prof. Li Ta-Kang, Chung Yuan Christian University, for their cordial advice.

REFERENCES

1. O. Sumita, A. Fukuda, and E. Hüge, *J. Appl. Polym. Sci.*, **23**, 2279 (1979).
2. F. Higashi, C. S. Cho, H. Kakinoki, and O. Sumita, *J. Appl. Polym. Sci.*, **15**, 2303 (1977).
3. C. C. Yen, T. C. Chang, and H. Kakinoki, *J. Appl. Polym. Sci.*, **40**, 53 (1990).
4. C. C. Yen, C. J. Huang, and T. C. Chang, *J. Appl. Polym. Sci.*, to appear.
5. J. March and S. Windwer, *General Chemistry*, Macmillan, New York, 1979, p. 501.
6. D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 3rd Ed, Holt, Rinehart and Winston, New York, 1976, pp. 780-782.

Received November 30, 1989

Accepted August 21, 1990