

Studies on the Preparation and Properties of Conductive Polymers. VII. Use of Two-Stage Method to Prepare Ag–Hg Alloy on Polymer Films

LIANG-TAU CHANG and CHIH-CHAO YEN*

Department of Chemical Engineering, Ming Hsin Institute of Technology and Commerce, Hsin Feng, Hsin Chu, Taiwan 304, Republic of China

SYNOPSIS

Polymer metal chelate films were prepared by silver nitrate mixed with polymers containing functional groups such as poly(vinyl alcohol) (PVA) by using two-stage method to prepare Ag–Hg alloy on polymer films. In the first stage, polymer silver chelate was treated with doping agents. In the second stage, these treated films were further treated with Hg metal. After the two stage treatment, films with good electrical conductivity can be obtained.

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INTRODUCTION

Lee et al.^{1,2} proposed a novel method for preparing Ag–Hg alloy-metallized polyacrylamide (PAAm) film by holding a PAAm–Ag⁺ aqueous solution under a Hg-saturated atmosphere at room temperature. However, this method cannot be applied to any other polymer metal chelate films, including poly(vinyl alcohol) (PVA)–Ag⁺ chelate films.

In the previous articles of this series,^{3–7} 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 PVA, polyamide, and polyamide–imides (PAI). These polymer metal chelate films were reduced by reducing agents or the retroplating-out method.

When polymer metal chelate films cannot be metallized by a one-step process, such as reduction by reducing agents or the retroplating-out method, the two-stage method to prepare metallized polymer films can be utilized. This experimental method and results were reported in a previous article of this series.⁸

Lee et al. reported that PVA–AgNO₃ chelate film cannot form Ag–Hg alloy on the film surface when

directly treated with Hg metal.¹ In this investigation, the two-stage method was used again to prepare γ -phase Ag–Hg alloy on PVA film surfaces and it exhibited excellent conductivity comparable to the Ag–Hg alloy on PAAm film as mentioned above.^{1,2}

EXPERIMENTAL

Preparation of γ -Phase Ag–Hg Alloy on PVA Films by the Two-stage Method

The PVA–AgNO₃ chelate films were prepared by the method reported in a previous paper of this series.³ The films of the Ag–Hg alloy on PVA were prepared by the two-stage method. In the first stage, somewhat wet 25% PVA–AgNO₃ chelate films (wt % AgNO₃ based on PVA weight) were dipped into a 6 wt % ethanol solution of I₂ for about 5 s and air-dried for a few minutes, repeating the above procedure three times. In the second stage, we dropped Hg metal onto the iodine-treated film surface for several days in a dry box with silica gel. The Ag–Hg alloy on PVA film was obtained.

Electric Measurement

The surface electrical conductivities of the iodine- and Hg-treated PVA films were measured according to the conventional four-terminal method, using

* To whom correspondence should be addressed.

aluminum foil electrodes as described in a previous paper.³

Instrument Analysis

Morphology of the iodine- and Hg-treated PVA film surface was observed under a Hitachi Model S-570 scanning electron microscope (SEM). The SEM specimens were prepared by evaporating gold onto the film surface after drying under vacuum. X-ray diffraction patterns of the iodine- and Hg-treated PVA films were measured by a Shimadzu XD-3A diffractometer, using $\text{CuK}\alpha$ radiation generated at 30 kV and 20 mA.

RESULTS AND DISCUSSION

The Ag-Hg alloy polymer films were prepared by a two-stage method in this study. In the first stage, PVA-AgNO₃ chelate films were treated with doping

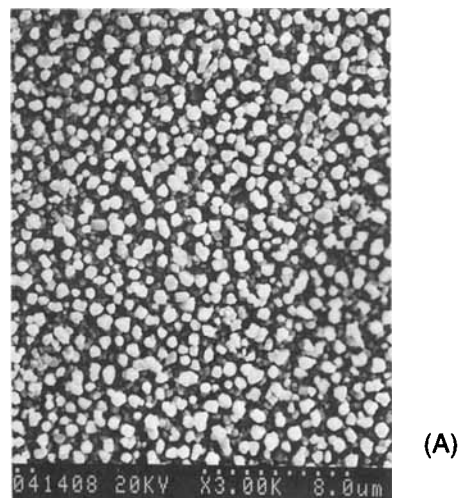
Table I Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Peaks Observed in X-ray Analysis for PVA-AgNO₃ Chelate Films Treated with I₂/EtOH Solution and Subsequently with Hg Metal

Peaks	Film A ^a Experiment		Pure AgI Reference	
	2θ	d	2θ	d
1	22.1	4.020	22.32	3.980
2	23.6	3.770	23.71	3.750
3	25.1	3.540	25.35	3.510
4	39.0	2.307	39.20	2.296
5	42.4	2.130	42.63	2.119
6	46.1	1.967	46.31	1.595

Peaks	Film B ^b Experiment		Pure γ -Phase Ag-Hg	
	2θ	d	2θ	d
1	31.1	2.871	31.0	2.880
2	33.6	2.663	33.5	2.670
3	38.4	2.344	38.1	2.360
4	40.2	2.244	40.2	2.244
5	46.2	1.963	46.2	1.965
6	55.2	1.663	55.0	1.667
7	63.0	1.475	62.8	1.478
8	69.1	1.358	68.7	1.365
9	77.5	1.230	77.1	1.236

^a Film A prepared from PVA-AgNO₃ chelate film treated with I₂/EtOH solution only.

^b Film B prepared from film A treated with Hg metal.



(A)



(B)

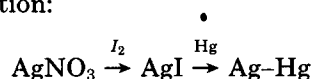
Figure 1 Scanning electron microscope photographs of the PVA-Ag⁺ chelate film treated with I₂ and Hg.

agents, such as an ethanol solution of I₂. These films showed surface resistivity in the range of 10⁴-10⁵ Ω/cm². These treated films were further treated with Hg metal in the second stage and they exhibited low surface resistivity around 10⁻¹ Ω/cm².

X-ray Analysis

The PVA-AgNO₃ chelate films were treated with iodine and Hg. The change of the surface substance

on the films is proposed to be reflected by the following equation:



To confirm that the change of surface substance on the films is exactly as the equation mentioned above, these films were examined by means of X-ray diffraction.

As shown in Table I, the PVA-AgNO₃ chelate films were treated with iodine; the light yellow substance that appears on the film surfaces was shown to be AgI by means of X-ray analysis. Subsequently, the AgI on the treated surfaces was converted to the γ -phase Ag-Hg alloy when these films were further treated with Hg metal in the second stage. The above results indicate that the change of surface substance on the film was exactly as depicted by the equation mentioned above.

SEM Observations

Scanning electron microscope (SEM) photographs display particles of AgI that are aggregated on the surfaces of iodine-treated PVA-AgNO₃ film, as shown in Figure 1 (a). When these treated films were further treated with Hg, the γ -phase Ag-Hg alloy forms a continuous distribution, as shown in Figure 1 (b). The continuous distribution on the film surface was believed to be responsible for the improvement of electrical conductivity. The iodine-treated PVA-AgNO₃ film exhibited higher surface resistivity

(10^4 – $10^5 \Omega/\text{cm}^2$) due to AgI itself not having very high conductivity and the globular AgI particles being distributed on the surface of the PVA film in an "islands" state.

In this investigation, the two-stage method was utilized when polymer metal chelate films cannot be obtained by a one-step process. The two-stage method might be utilized for other functional polymer metal chelate films.

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