

Novel Method to Prepare Conductive Coatings from Metal Chelate of Polyester

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Abstract

The conductive polyvinyl acetate (PVAc) chelate coatings were prepared by spreading various mixtures of transition-metal salts (AgNO_3 , CuCl_2 , NiCl_2 and CoCl_2) and polyvinyl acetate in formic acid solution onto PET sheet substrates and dried by heat treatment and reduced with sodium borohydride aqueous solution, which were found to have surface resistivity less than $1 \Omega/\text{cm}^2$. The IR spectra and the viscosity of the metal chelate mixtures, as well as the SEM of the coating surfaces before and after reduction were studied. The PVAc-metal chelate coatings not only had good adhesion to the substrates, but also exhibited stable and excellent conductivity. And by means of X-ray diffraction analysis, these reduced coatings were shown to have metallized surfaces that were believed to be responsible for the excellent conductivity.

Key Word : Conductivity Coating, Metal Chelate, Polyvinyl Acetate, Surface Resistivity

1. INTRODUCTION

In the recent years, the substantial advance in manufacturing technology of integrated circuits has brought out large demands on the special handling protection for these electronic products¹⁻³. These demands have attracted growing interest on the research of conductive polymers and coatings^{4,5}. One approach to prepare conductive polymers is to add conductive fillers, such as powders of silver, nickel, carbon, etc., into the insulator resins to increase their conductivity⁶⁻⁹. The main drawback of this technique is that it requires a large amount of fillers to be added into the resins. This inevitably reduces the mechanical strength, pliability and adhesion of the resulting conductive polymers. The other approach is by forming chelates between metal salts and the functional groups of the polymers¹⁰⁻¹⁵.

In this paper, characterization of the conductive coatings prepared from adhesive polyvinyl acetate (PVAc) and various metal salts via chelate formation approach is reported. This includes viscosity measurement, infrared spectroscopy, X-ray diffraction, and scanning electron microscope inspection. The PVAc-metal chelate coatings not only had good adhesion to the substrates, but also exhibited stable and excellent conductivity. It is believed that these conductive coatings may have potential applications in providing static charge conduction for electronic products.

2. EXPERIMENTAL

2.1 Preparation of PVAc-metal chelate coatings

The PVAc-metal chelate mixtures were prepared by introducing the metal salt solution into a 15-20wt% PVAc formic acid solution according to the predetermined weight ratios (w%) of the metal salts to the PVAc. The metal salts used were AgNO_3 , CuCl_2 , NiCl_2 and CoCl_2 . The mixtures were stirred at room temperature for 24 hours. The resulting viscous mixtures were then uniformly

spread onto the sheet substrates made of PET. The coated substrates were dried by an electrical oven with forced air circulation at 80°C for 20 minutes. The colors of the dried coatings prepared from different metal salts are listed in Table 1.

2.2 Metallization of PVAc-metal chelate coatings

Metallization of the dried coatings was conducted according to the method previously reported¹²⁻¹⁵. The dried coatings were treated with various concentrations of NaBH₄ aqueous solutions for suitable periods of time and appropriate temperature to allow for optimum reduction. The temperature ranged from 30 to 70°C and the treatment times extended from 1 to 10 minutes. The coating surfaces displayed metallic luster after the reduction. The reduced coatings were washed repeatedly with distilled water and dried in a vacuum oven at 80°C for 24 hours to a constant weight, then cooled down to room temperature and stored in a desiccator for further experiments.

2.3 Characterization of PVAc-metal chelates

2.3.1 Viscosity measurement

The viscosity of the PVAc metal chelate mixtures was measured by Brookfield Viscometer/ Rheometer (Model RVDV-III) maintained at 25°C.

2.3.2 Infrared spectroscopy

Infrared spectra of the PVAc metal chelates were analyzed by Shimadzu Fourier transform infrared spectrophotometer (FTIR 8300): All the spectra were recorded within the wavenumber range 4000-400cm⁻¹ at 25°C.

2.3.3 Electrical properties

Electrical surface resistivity (Rs) of the coatings before and after reduction was measured by the four-terminal method using a multimeter (model YF-2000) when it was under 10⁷Ω/cm² and was measured by a high resistance meter (model

HP4337A) when it was above $10^7 \Omega/\text{cm}^2$.

2.3.4 X-ray diffraction

A MAC Science MXPIII diffractometer was used to analyze the X-ray diffraction patterns of the unreduced and reduced coating layers by using $\text{CuK}\alpha$ radiation generated at 40keV and 30mA.

2.3.5 Scanning electron microscope inspections

The surfaces of these coatings before and after reduction were inspected by a TOPCON SM-300 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1 Coordination of PVAc-metal chelates

The characteristic colors of the PVAc-metal chelates are summarized in Table 1. As pointed out in the previous studies¹²⁻¹⁴, these characteristic colors were resulted from the coordinate bond formation between the polymer and the metal ions. In order to confirm the coordination and understand its rheological effect, the IR spectra and the viscosity of these PVAc-metal chelates were further investigated.

3.1.1 Infrared spectra analysis

Figure 1 shows the changes of the IR spectra of PVAc after complexation with CuCl_2 (w%=15%), NiCl_2 (w%=15%) and AgNO_3 (w%=3%). It is obvious that the pure PVAc have two characteristically strong absorption bands arising from $\text{C}=\text{O}$ stretching vibration (at 1750 cm^{-1}) and $\text{C}-\text{O}$ stretching vibration (at 1211 cm^{-1} and 1022 cm^{-1}). However, both of the PVAc-Cu and the PVAc-Ni chelate have their $\text{C}=\text{O}$ stretching vibration shifted to lower frequency and extended into a broader absorption band, and the $\text{C}-\text{O}$ stretching bands (1211 cm^{-1}

and 1022cm^{-1}) shifted to higher frequencies and broaden. Because the PVAc-Ag chelate is dark brown in color, a lower concentration of AgNO_3 ($w\%=3\%$) was used to increase the IR transmittance, and the changes of the spectra of the PVAc-Ag chelate was similar to those of the PVAc-Cu and the PVAc-Ni chelates. These observations confirm the chelate formation for metal ions coordinated with carbonyl groups of PVAc.

3.1.2 Viscosity analysis

Figure 2 shows the effects of shear rate on the viscosity of PVAc-Ag chelate mixtures of various AgNO_3 concentrations. It can be observed from the curves that the PVAc solution and the PVAc-metal chelate mixtures are pseudoplastic fluids, of which the viscosity decreases with the increase of shear rate. Also, the viscosity of PVAc-Ag solution decreased with the increase of AgNO_3 concentration and all have lower viscosity than that of the pure PVAc solution. When PVAc-Cu chelate mixtures were used, the same phenomena were observed and the results are shown in Figure 3. From these results, it is evident that the chelate formation in PVAc-metal chelate mixtures reduced the tangle of the PVAc polymer molecules.

3.2 Electrical properties of PVAc-metal chelates

As shown in Table 2, the PVAc-metal chelate coatings had different electrical conductivity when different metal salts were used. Before reduction, the surface resistivity of the PVAc-Ag chelate coatings was about $1 \times 10^4 \Omega/\text{cm}^2$. After moderately reduced with a $0.4\text{wt}\%$ NaBH_4 aqueous solution at 40°C for 2 minutes, the surface resistivity was largely reduced to about $1 \Omega/\text{cm}^2$, which is the minimum value that can be measured by the four terminal method. The surface resistivity of the PVAc-Cu chelate coatings was also reduced to about $10^3 \Omega/\text{cm}^2$ after treated with a $4\text{wt}\%$ NaBH_4 aqueous solution. But when a stronger condition of $10\text{wt}\%$ NaBH_4 solution at 65°C for 10 minutes was used, the improvement on the surface resistivity of the PVAc-Ni and the PVAc-Co chelate coatings was less than expected. When a much higher temperature and a longer reduction time were

used, the surface structure of these PVAc-Ni and PVAc-Co chelate coatings was destroyed before any improvement of the surface resistivity could be attained.

3.3 X-ray diffraction analysis

X-ray diffraction analysis was used to understand the changes induced on the surfaces of the PVAc-Ag (w%=15%) chelate coatings after treatment of the NaBH_4 solution. The results are summarized in Table 3. The distinct diffraction peaks indicate that the main product on the reduced coating surfaces was metallic silver. It is believed that the formation of metallic silver on the surface is responsible to the excellent conductivity of these reduced coatings.

3.4 Scanning Electron Microscope Inspections

The surface condition of the PVAc-Ag (w%=15%) chelate coatings was further investigated by scanning electron microscope. As shown in Figure 4, the surface appearances were drastically changed after treated with NaBH_4 , as compared with those of the pure PVAc and the unreduced PVAc-Ag (w%=15%) chelate coatings. Figure 4 (a) is a SEM photograph (magnification 150x) showing an extremely rough surface of the reduced PVAc-Ag chelate coating. Figure 6(b) is a SEM photograph (magnification 7000x) from which one can find that much more particles or crystals of metallic silver were aggregated on the surface of the reduced PVAc-Ag chelate coating to form a connecting network. It is the formation of this conducting network makes major contribution to the excellent conductivity of the reduced coatings.

4. CONCLUSION

The IR spectra of the PVAc metal chelates confirmed that the metal ions, such as Ag^+ , Cu^{2+} , Ni^{2+} , Co^{2+} , etc., coordinate with carbonyl group of the PVAc polymer in chelate formation. The SEM and X-ray analysis revealed that a network linkage of conductive metal particle was formed on the surface of the

PVAc-metal chelate coating after the treatment of NaBH_4 solution. This metallic layer plays an important role to improve the conductivity of the coatings. Besides, the chelate structure provides a stabilizing effect on the metallic layer so that the latter can adhere firmly to the coatings surface. The reduced PVAc-Ag chelate coatings exhibit stable and excellent conductivity.

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Table 1. Colors of various PVAc-metal chelate coatings ^a.

Metal salt(w%=15%) ^b	Thickness (mm)	Color
-	0.05	transparent
AgNO ₃	0.1	dark brown
CuCl ₂	0.1	yellowish green
NiCl ₂	0.1	lemon
CoCl ₂	0.1	pink

- a. All coatings were spread on PET substrates, dried and without NaBH₄ treatment.
 b. Concentrations of the metal salts were w%=15% based on the PVAc weight.

Table 2. Effect of metal salt species on the conductivity of PVAc-metal chelate coatings.

Metal salts ^a	Rs (Ω/cm^2)	Rs (Ω/cm^2)
-	1.21×10^{15}	1.21×10^{15}
AgNO ₃	1.10×10^4	1.00×10^0 ^b
CuCl ₂	1.30×10^{11}	1.00×10^3 ^c
NiCl ₂	1.50×10^{10}	5.60×10^7 ^d
CoCl ₂	5.00×10^7	2.00×10^7 ^d

- a. Based on the PVAc weight.
 b. Concentration of NaBH₄ solution=0.4wt%, temperature=40°C, time=2 min.
 c. Concentration of NaBH₄ solution=4.0wt%, temperature=50°C, time=2 min.
 d. Concentration of NaBH₄ solution=10.0wt%, temperature=40°C, time=2 min.

Table 3. Diffraction angles (2θ) and plane distances (d) corresponding to the observed peak in X-ray analysis for PVAc-Ag ($w\%=15\%$) chelate coating reduced by NaBH_4 agent.

Peaks	Coating layer		Pure Ag reference	
	2θ	d	2θ	d
1	38.0	2.359	38.12	2.359
2	44.12	2.051	44.27	2.043
3	64.58	1.442	64.42	1.445
4	77.54	1.230	77.47	1.230

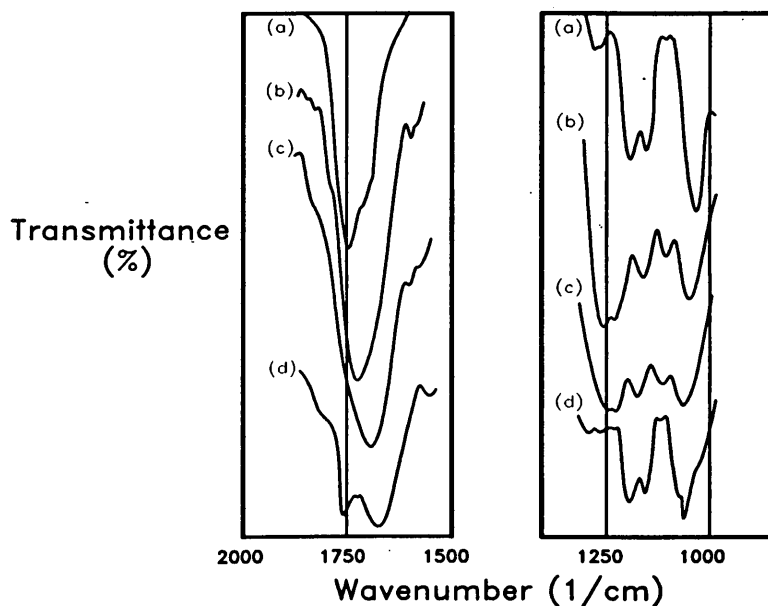


Fig.1 Diffused reflectance FTIR spectra of various PVAc-metal chelates. (a) Pure PVAc; (b) PVAc- CuCl_2 ($w\%=15\%$); (c) PVAc- NiCl_2 ($w\%=15\%$); (d) PVAc- AgNO_3 ($w\%=3\%$).

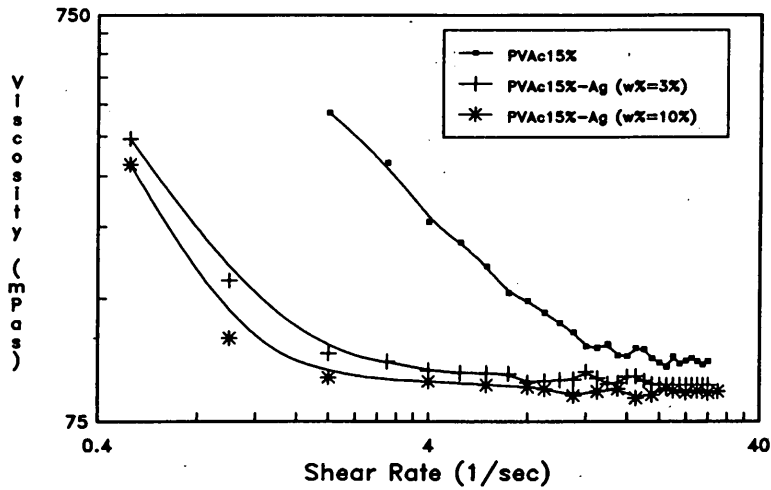


Fig. 2 Effect of shear rate on the viscosity of PVAc-Ag chelate mixtures of various AgNO_3 concentrations.

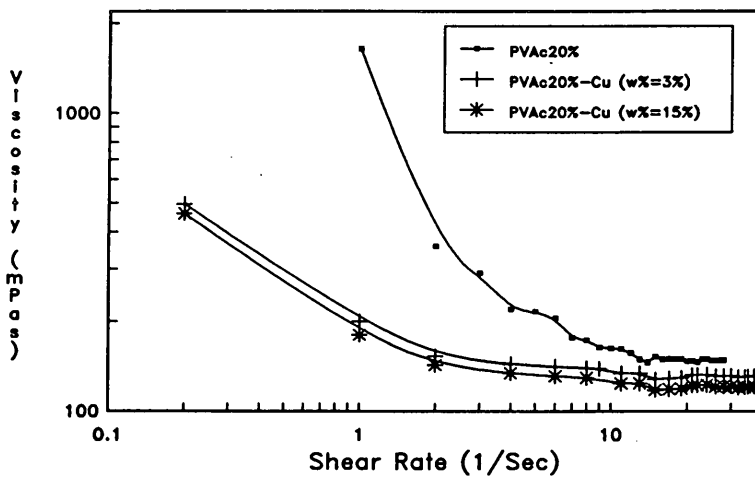
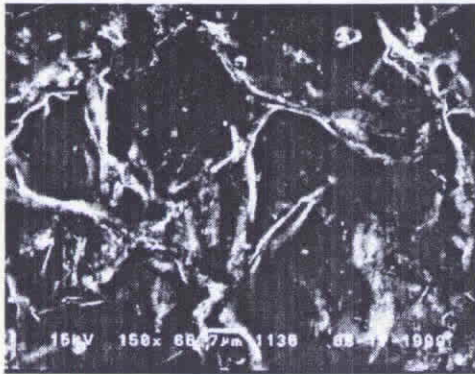
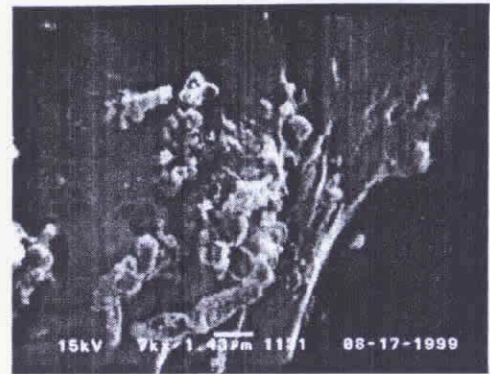


Fig. 3 Effect of shear rates on the viscosity of PVAc-Cu chelate mixtures of various CuCl_2 concentrations.



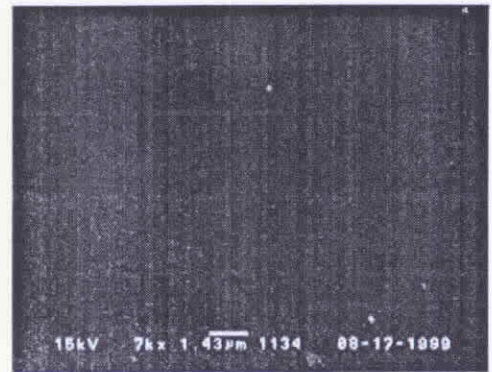
(a)



(b)



(c)



(d)

Fig.4 Scanning electron microscope photographs showing variation of the surfaces of PVAc-Ag(w%=15%) chelate coatings. (a) After NaBH_4 treatment (150x), (b) After NaBH_4 treatment (7000x), (c) Before NaBH_4 treatment (7000x), (d) Pure PVAc coating (7000x).

聚酯金屬螯物導電性塗料之新穎製備法

黃鵠容 劉宗宏

摘 要

本研究開發一系列新型之聚醋酸乙烯酯金屬螯物導電塗料，並研究此型塗料之導電性質與製造方法。本研究利用具黏著性質的聚醋酸乙烯酯聚合體和過渡金屬鹽類(AgNO_3 , CaCl_2 , NiCl_2 和 CoCl_2 等)製成聚醋酸乙烯酯金屬螯合溶液，將此溶液塗佈在 PET 的基板上，經過乾燥及硼氫化鈉的還原後，基板上塗層的表面電阻可達到 $1\ \Omega/\text{cm}^2$ 以下。還原後之塗層經由 SEM 和 X-ray 之分析數據，確定塗層表面有金屬之形成，這層均勻的金屬層是塗料具有優良導電度的原因。本研究並利用 FTIR 光譜分析和黏度分析來測定螯合物的生成結構。本研究方法所製成的金屬螯物塗料除了導電性優異外，對基材亦有良好的黏著性。

關鍵字：導電塗料、聚醋酸乙烯酯、表面電阻、導電度