

# Metallization of Crosslinked Acrylate Resin by Reduction of Polymer-Incorporated Metal Ion

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**ABSTRACT:** Crosslinked acrylate resin were prepared by the radical polymerization of poly(ethylene glycol) diacrylate (ADE400) with 2,2'-azobisisobutyronitrile in the presence of cobalt (II) chloride at 100°C for 48 h. Metallization behavior of the CoCl<sub>2</sub>-containing acrylate resin by reduction with aqueous sodium tetrahydroborate solution at 25°C was investigated by means of infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and electron probe microanalysis. As a result, the surface of the

crosslinked acrylate resin was successfully metallized by the reduction, and the cobalt layer generated at the side of a polypropylene plate used in the preparation of film was thicker and smoother than the air side. Most of the chlorine ion in the film passed in the reduction solution. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3864–3868, 2004

**Key words:** metal-polymer complexes; surfaces; resins; ESCA/XPS; FT-IR

## INTRODUCTION

Metallization of a polymer surface, or plastics metallizing, is a kind of composite technology to obtain plastics with wide variation of surface properties without altering the bulk properties. The wet plating method known as electroless plating, the dry plating method known as vacuum deposition or metal spraying, and the coating method such as using a metallic paint are well known as techniques for metallization of polymer surface.<sup>1–2</sup> These techniques sometimes require preliminary surface treatment, such as mechanical roughing, chemical modification, etching, sensitizing, or activation. As a more convenient metallization technique, a novel method of reduction of polymer-incorporated metal ions<sup>3–12</sup> or polymer-metal chelates<sup>13–14</sup> with an aqueous solution of NaBH<sub>4</sub> was developed by a few groups. This method was known to be applicable to the surface metallization of highly polar linear polymers such as polyacrylonitrile, poly(vinylidene fluoride), poly(vinyl alcohol), polyamide, polyamide-imide, and polyurethane. Recently, we have found that the surface of the crosslinked epoxy<sup>15</sup> and urethane<sup>16</sup> resins containing polyethylene glycol unit can be metallized by this method. As the application of this method, the production of coating materials having metallic luster in addition to electronic materials is industrially very important. Acrylate resins are popular coating materials. The present study

describes the surface metallization of crosslinked acrylate resin prepared by the polymerization of poly(ethylene glycol) diacrylate (ADE-400) by reduction of polymer-incorporated cobalt ion.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) diacrylate (Blemer ADE-400, degree of polymerization for ethyleneoxy unit: ca. 9) was kindly supplied by NOF Corp. (Tokyo, Japan). Reagent-grade cobalt (II) chloride, 2,2'-azobisisobutyronitrile (AIBN), and sodium tetrahydroborate were used without further purification.

### Preparation of samples

Cobalt (II) chloride (3.90 g, 30.0 mmol) and AIBN (10 mg, 0.061 mmol) were added to ADE-400 (20.0 g), and then the mixture was stirred at room temperature for 24 h. The obtained solution was poured on a polypropylene plate at room temperature and heated at 80–100°C for 48 h to give a cured acrylate film. Metallization by reduction treatment was performed by dipping the cured film containing the cobalt chloride in a 0.05 wt % sodium borohydride aqueous solution at 25 or 55°C for 5–30 min, followed by washing with ethanol and subsequently with toluene and drying.

### Measurements

Surface resistance of the metallized films was determined by the conventional four-probe method by us-

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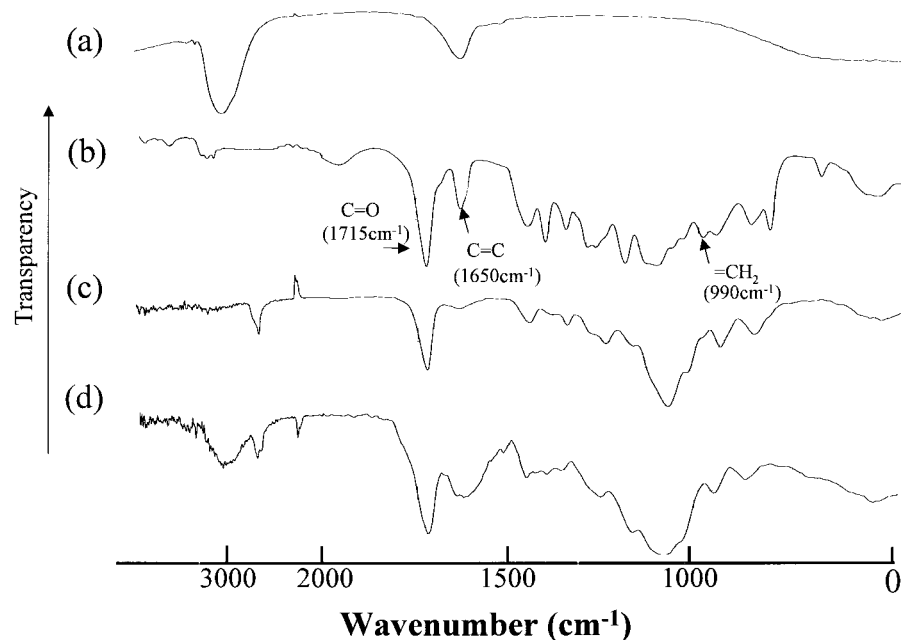


Figure 1 IR spectra of (a)  $\text{CoCl}_2$ , (b) ADE-400, (c) cured ADE-400 at  $100^\circ\text{C}$ , and (d) cured ADE-400/ $\text{CoCl}_2$  at  $100^\circ\text{C}$ .

ing a digital multimeter (Model R6871E, Advantest Co., Ltd.). Infrared (IR) spectra of the films with and without cobalt (II) chloride were measured on a Shimadzu 8100 FTIR spectrometer by ATR method. Dynamic viscoelastic measurements of the films were performed on a Rheograph Solid (Toyo Seiki Co., Ltd., Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of  $2^\circ\text{C}/\text{min}$ . Surface of the deposited metal layer was observed with a scanning electron microscope (JEOL JSM-6300, Japan Electron Co., Ltd.). The elemental distribution of metal in the film was observed by use of an electron probe microanalyzer (EPMA, JEOL Ltd., JXA-8800) with an accelerating voltage of 15.0 kV and probe current of  $0.01 \mu\text{A}$ . X-ray diffraction analysis of the deposited metal was carried out with an X-ray diffrac-

tometer (Rigaku Denki Co. Ltd., RINT-2100), using  $\text{CuK}\alpha$  radiation at 40 kV and 14 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a photoelectron spectrometer (JEOL Ltd., JPS-90SX) by using  $\text{MgK}\alpha$  radiation at 12 kV and 5 mA, after argon ion beam etching for 5 s (depth: ca. 5 nm) at the condition of accelerating voltage of 500 V and ion beam current of 50 mA to avoid contamination of the uppermost surface of the metallized film.

## RESULTS AND DISCUSSION

### Various properties of the crosslinked acrylate resin containing cobalt (II) chloride

As metal chloride adding to the crosslinking system of ADE-400 and AIBN at  $80\text{--}100^\circ\text{C}$ , cobalt (II) chloride, iron (II) chloride, and copper (II) chloride were exam-

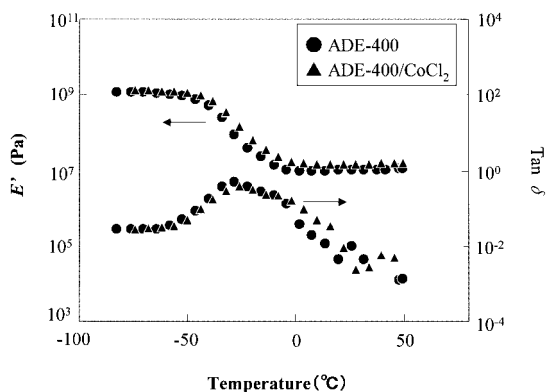


Figure 2 Dynamic viscoelastic curves of the ADE-400 and ADE-400/ $\text{CoCl}_2$  films cured at  $100^\circ\text{C}$ .

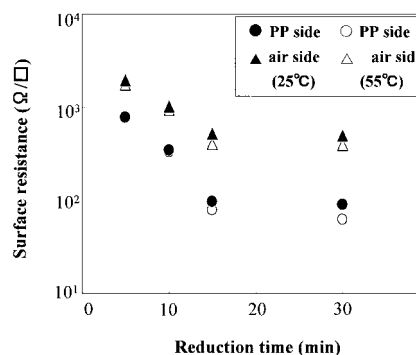


Figure 3 Relation between reduction time and surface resistance of the ADE-400/ $\text{CoCl}_2$  film cured at  $100^\circ\text{C}$ .

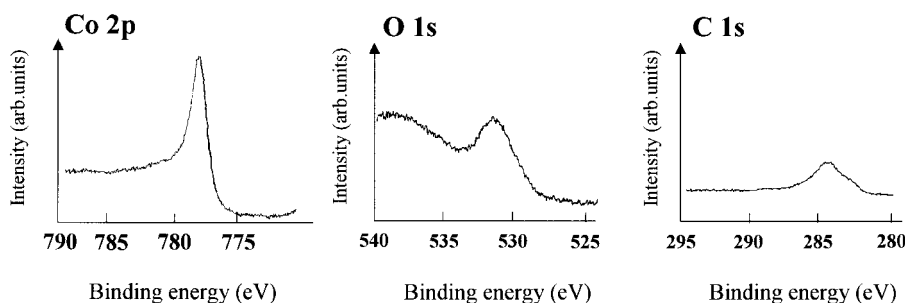


Figure 4 XPS spectra of the Co 2p<sub>2/3</sub>, O 1s, and C 1s regions of the metallized ADE-400 film at the air side.

ined. Although the iron and copper chlorides did not afford a fully cured resin, the cobalt chloride gave a satisfactory result. We do not know the clear reason, but it is thought that the former chlorides may disturb the radical polymerization by the action of some redox reactions. Progress of the curing reaction of ADE-400 in the presence of cobalt (II) chloride was identified by use of IR spectroscopy (Fig. 1). The absorption peak at 1650 cm<sup>-1</sup> assigned to the stretching of vinyl attached to carbonyl group and the peak at 990 cm<sup>-1</sup> corresponding to =CH<sub>2</sub> out-of-plane bending in the IR spectrum of ADE-400 disappeared in the spectrum of the cure ADE-400, indicating that the vinyl group of ADE-400 polymerized. The IR spectrum of the cured ADE-400/CoCl<sub>2</sub> can be represented by overlapping of the spectra of the cured ADE-400 and CoCl<sub>2</sub> (1650 cm<sup>-1</sup>), indicating that the crosslinking of ADE-400 certainly occurs in the presence of CoCl<sub>2</sub>.

Figure 2 shows the dynamic viscoelastic curves of the cured ADE-400 and ADE-400/CoCl<sub>2</sub> films. The storage modulus ( $E'$ ) of the cured ADE-400 and ADE-400/CoCl<sub>2</sub> films decreases around -40°C and gradually becomes almost constant (ca. 16 MPa). This result indicates that network polymer structure certainly formed in both the ADE-400 and the ADE-400/CoCl<sub>2</sub>

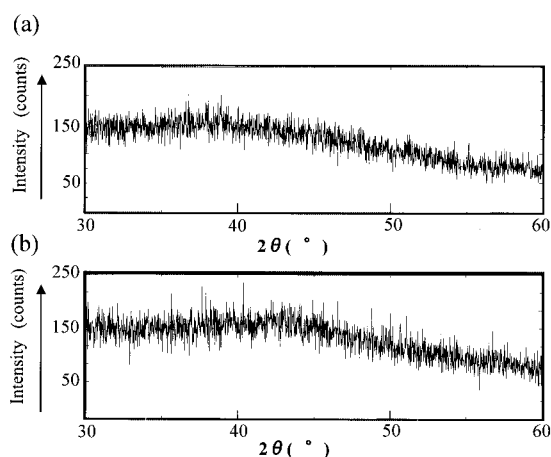


Figure 5 X-ray diffraction patterns of the metallized ADE-400 film: (a) air side and (b) PP side.

cured films and that the cobalt chloride does not disturb the crosslinking reaction of ADE-400. The tan  $\delta$  peak temperature (-26°C) of the cured ADE-400/CoCl<sub>2</sub> film was slightly higher than that of the cured ADE-400 film (-28°C), suggesting that some interaction between crosslinked acrylate resin and cobalt (II) chloride occurred.

#### Surface metallization of the crosslinked acrylate resin containing cobalt (II) chloride

The reduction of the crosslinked acrylate resin containing cobalt (II) chloride with aqueous sodium borohydride at 25 or 55°C successfully afforded a film with metallic luster. The change of surface resistance of the metallized ADE-400 film is shown in Figure 3. The insulated film before reduction became a surface conductive film after reduction. The surface resistance decreased with increasing reduction time until 15 min

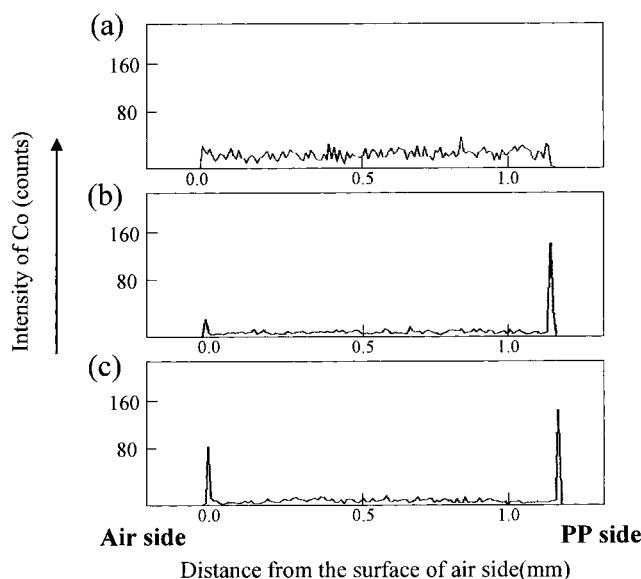
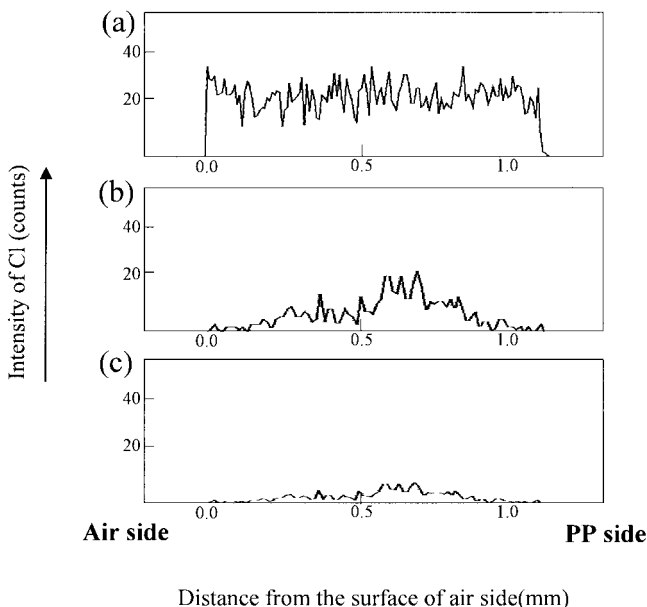


Figure 6 Elemental distribution of Co by EPMA line analysis in the depth direction of the cured ADE-400/CoCl<sub>2</sub> film (reduction temperature: 25°C) as a function of reduction time: (a) 0 min (before reduction), (b) 3 min, and (c) 15 min.

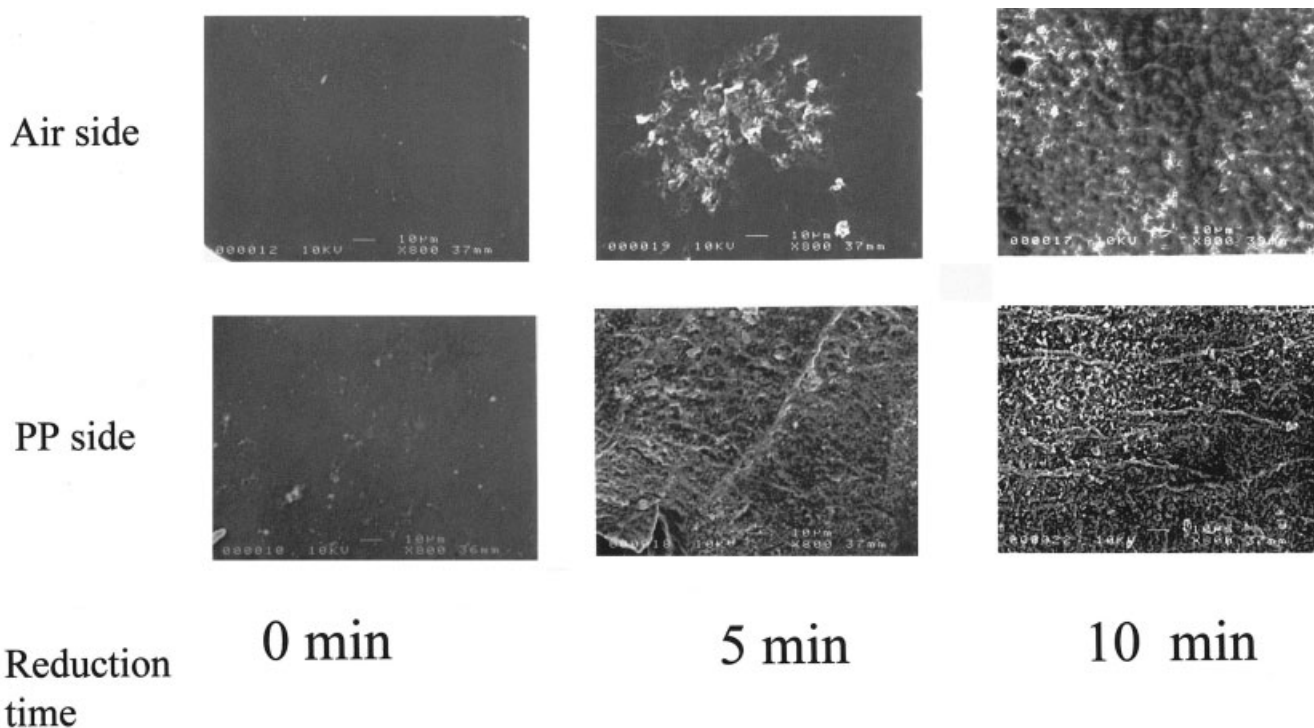


**Figure 7** Elemental distribution of Cl by EPMA line analysis in the depth direction of the cured ADE-400/CoCl<sub>2</sub> film (reduction temperature: 25°C) as a function of reduction time: (a) 0 min (before reduction), (b) 3 min, and (c) 15 min.

and then became almost unchanged, indicating the reduction is almost completed at 15 min in both the cases of 25 and 55°C. The increase of reduction temperature caused a slight decrease of surface resistance.

Surface resistance at the polypropylene side was lower than that at air side.

Figure 4 shows XPS spectra of the air side of the metallized ADE-400 film. The intense peak at 778.5 ppm is assigned to the pure Co(2p<sub>3/2</sub>) metal and the peaks related to C 1s and O 1s of acrylate resin were weak, indicating that the metal ion migrates to the surface and is reduced to pure metal. The polypropylene side surface of the metallized ADE-400 film showed almost the similar spectra. Figure 5 shows X-ray diffraction pattern of the metallized ADE-400 film. A small peak related to a crystalline cobalt was observed on both sides, indicating that the formed metal is almost amorphous. The generated metal may have defects in the lattice or contain some impurities. Figures 6 and 7 show typical change of the elemental distribution of Co and Cl, respectively, in the depth direction of the film (thickness: ca. 1.2 mm) during the reduction obtained by EPMA line analysis. Cobalt ion was homogeneously distributed in the inner part of the film before reduction and migrated to the polymer surface by the reduction treatment, becoming more densely distributed on the polymer surface at the polypropylene side. On the other hand, chlorine ion migrated to the film surface and almost disappeared in the film at 15 min. From the results of EPMA and XPS, it is obvious that cobalt ion migrates to the film surface and reduced to cobalt metal by the reaction with sodium tetrahydroborate solution, and the chlo-



**Figure 8** SEM micrographs of the surface of the metallized films as a function of reduction time.

rine ion finally passed in the reduction solution. Figure 8 shows the SEM micrographs of the surface of metallized film as a function of reduction time. Cobalt particles are partially deposited on the air side surface, while already homogeneously deposited on the polypropylene side surface at the reduction time 5 min. Cobalt particles are more densely deposited at the polypropylene side than the air side at 10 min, in agreement with the result of surface resistance. We do not know the reason cobalt metal is more easily deposited on the polypropylene side surface, but the difference of the surface state may affect the metallization behavior.

### CONCLUSION

The cobalt ion incorporated in the acrylate resin which was prepared by the crosslinking reaction of poly(ethylene glycol) diacrylate at 100°C smoothly migrated to both sides of the film and then reduced to pure metal by dipping the film in aqueous NaBH<sub>4</sub> solution at 25°C for 15–30 min. The surface of the reduced film had metallic luster and the surface resistance reached 60 Ω/□. The XPS and X-ray diffraction analysis revealed that the generated cobalt is pure metal and almost amorphous. The EPMA and SEM measurements revealed that cobalt metal more densely deposited at the polypropylene side than at the air side. This metallization of acrylate resin may be applicable to some field of coating materials having electric conductivity and metallic luster.

### References

1. Mittal, K. L.; Susko, J. R. *Metallized Plastics 1: Fundamental and Applied Aspects*; Plenum Press: New York, 1989.
2. Mallory, G. O.; Hajdu, J. B. *Electroless Plating: Fundamentals and Applications*; American Electroplaters and Surface Finishers Society/William Andrew Inc.: Orlando, FL, 1990.
3. Yosomiya, R.; Hirata, M.; Morimoto, K.; Marutuka, T. *Jpn. Pat.* 274,778, 1988.
4. Yosomiya, T.; Ono, H.; Yosomiya, R. *Angew Makromol Chem* 1992, 197, 749.
5. Yosomiya, T.; Sato, Y.; Yosomiya, R. *Angew Makromol Chem* 1993, 206, 209.
6. Shibata, M.; Yosomiya, R.; Yosomiya, T. *Angew Makromol Chem* 1997, 253, 183.
7. Haga, Y.; An, H.; Sato, Y.; Yosomiya, R.; Yosomiya, T. in Mittal K. L. (Eds.) *Metallized Plastics: Fundamentals and Applications*; Marcel Dekker Inc.: New York, 1998; p. 85.
8. Shibata, M.; Beniya, H.; Yosomiya, R.; Yosomiya, T. *J Polym Res* 2000, 7, 57.
9. Yen, C.-C.; Chang, T.-C.; Kakinoki, H. *J Appl Polym Sci* 1990, 40, 53.
10. Yen, C.-C.; Huang, C.-J.; Chang, T.-C. *J Appl Polym Sci* 1991, 42, 439.
11. Huang, C.-J.; Yen, C.-C.; Chang, T.-C. *J Appl Polym Sci* 1991, 42, 2237.
12. Huang, C.-J.; Yen, C.-C.; Chang, T.-C. *J Appl Polym Sci* 1991, 42, 2267.
13. Nakamae, K.; Mohamed, N. A. *Polymer* 1993, 34, 1310.
14. Mohamed, N. A.; Nakamae, K. *Metallized Plastics: Fundamentals and Applications*; Marcel Dekker Inc.: New York, 1998; p. 27.
15. Shibata, M.; Uda, T.; Yosomiya, R. *Thin Solid Films* 2003, 440, 123.
16. Shibata, M.; Ito, T. *Polymer* 2003, 44, 5617.