

# Metallization of UV-Cured Acrylate Resins by Reduction of Polymer-Incorporated Cobalt Ion

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**ABSTRACT:** The surface of UV-cured films of poly(ethylene glycol) diacrylate (PEGAc)/tetrahydrofurfuryl acrylate (THFAc) (weight ratio 100/0, 90/10, and 80/20) was metallized by the reduction of polymer-incorporated cobalt chloride with aqueous sodium borohydride at 20°C. The electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy measurement revealed that the cobalt ion, which was homogeneously distributed in the inner part of the film before reduction, migrated to both sides of the film, and then reduced to pure metal by the reduction treatment. The surface resistance of the UV-cured PEGAc/THFAc film increased with increasing THFAc content. Especially, the trend was prominent at the glass side of the metallized films.

The glass transition temperature of the cured resin measured by dynamic viscoelastic analysis slightly rose with an increase of THFAc content. The EPMA map of cobalt and carbon in the depth direction of the metallized film showed that the cobalt layer, generated at the glass side of the film with a higher THFAc content, contains more polymer component, in agreement with the order of surface resistance. The X-ray diffraction analysis of the reduced films revealed that the degree of crystallinity of the generated cobalt was low. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1627–1632, 2006

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

## INTRODUCTION

Metallization of a polymer surface, or plastics metallizing, is a kind of composite technology to obtain plastics with a 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 techniques for metallization of polymer surface.<sup>1,2</sup> These techniques sometimes require preliminary surface treatment, such as mechanical roughening, chemical modification, etching, sensitizing, or activation. As a more convenient metallization technique, a novel method, by 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>, has been 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 thermosetting resins, such as epoxy,<sup>15</sup> urethane,<sup>16</sup> and acrylate<sup>17</sup> resins, containing polyethylene

glycol unit can be metallized by this method. If this method is applied to photocuring resins, it is possible to produce photocuring coating materials with metallic luster, which has many industrial applications. Acrylate resins having alkylene oxide units are popular UV-curing coating materials. The present study describes the surface metallization of UV-cured acrylate resins, derived from poly(ethylene glycol) diacrylate (PEGAc) and tetrahydrofurfuryl acrylate (THFAc), by reduction of polymer-incorporated cobalt ion.

## EXPERIMENTAL

### Materials

PEGAc (Blemer ADE-400, degree of polymerization for ethyleneoxy unit: ca. 9) was kindly supplied by NOF Corp. (Tokyo, Japan). THFAc (SR-285) and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, mp: 45–49°C) were kindly supplied from Nippon Kayaku Co. Ltd. (Tokyo, Japan) and Chiba Specialty Chemicals K.K. (Tokyo, Japan), respectively. Reagent-grade cobalt(II) chloride and sodium tetrahydroborate were used without further purification.

### Preparation of samples

Cobalt(II) chloride (324 mg, 2.50 mmol) was added to PEGAc (5.0 g), and then the mixture was stirred at room temperature for 24 h. Irgacure 184 (200 mg, 0.979

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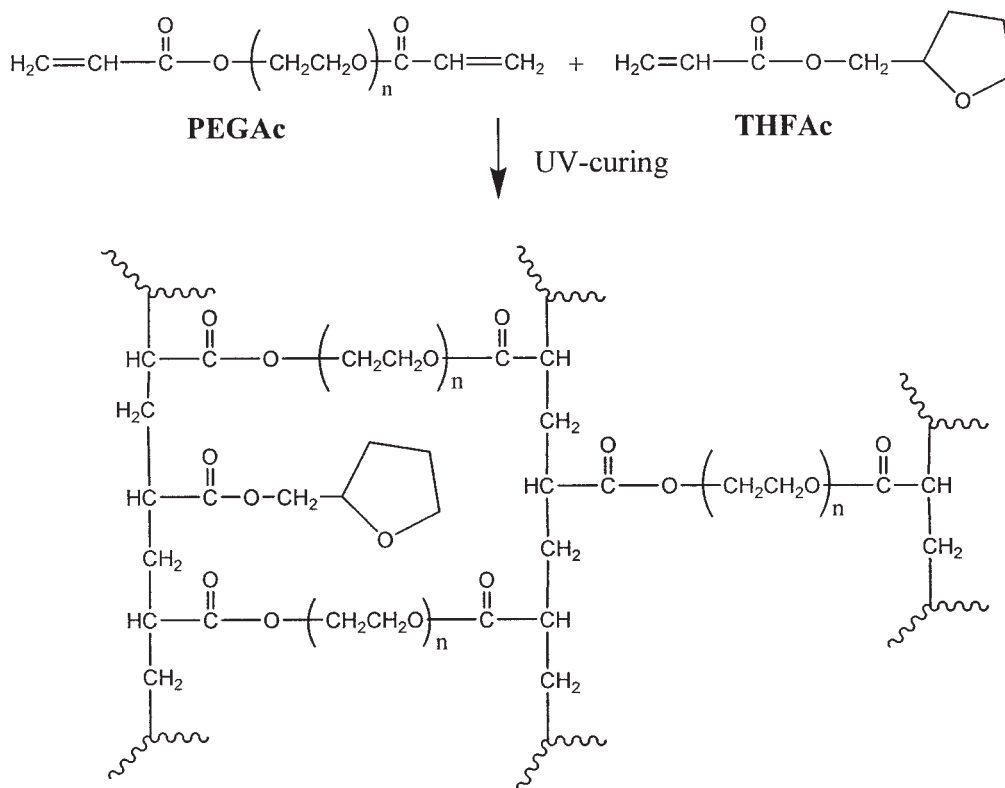


Figure 1 Probable UV-curing reaction of PEGAc and THFAc.

mmol) was added to the PEGAc/CoCl<sub>2</sub> solution, and then poured on a 85-mm  $\Phi$  culture dish, and UV-cured at room temperature for 60 s to give a cured acrylate film (thickness, ca. 0.4 mm). SPOT-CURE SP-7 (250 W light source; wavelength 240–440 nm; Ushio Inc., Yokohama, Japan) was used for the UV-curing (irradiation distance, 150 mm; irradiation intensity, 5 mW/cm<sup>2</sup>). Metallization by reduction treatment was performed by dipping the CoCl<sub>2</sub>-containing film peeled off from the culture dish in a 0.05 wt % sodium borohydride aqueous solution, at 25°C for 5–30 min, followed by washing with ethanol and subsequently with toluene, and dried.

The metallized PEGAc/THFAc (90/10 and 80/20) blend films were prepared in a similar manner as mentioned earlier, except for using PEGAc/THFAc of 4.5 g/0.5 g and 4.0 g/1.0 g. The probable crosslinking reaction of PEGAc and THFAc was shown in Figure 1.

### Measurements

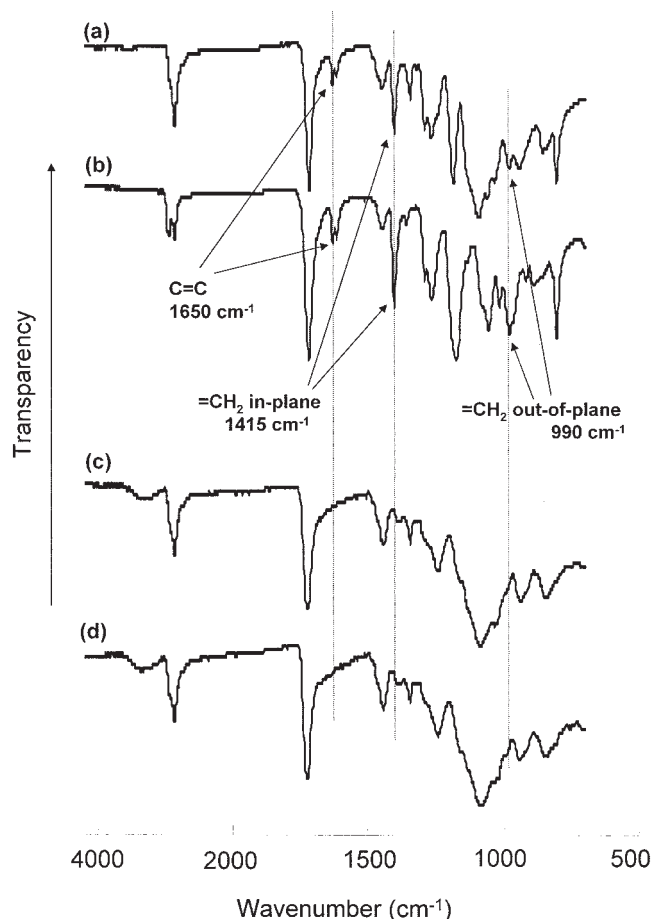
Surface resistance of the metallized films was determined by the conventional four-probe method, using a digital multimeter (Model R6871E, Advantest Co., Ltd.). Infra-red (IR) spectra of the acrylate resin films and cobalt(II) chloride were measured on a Shimadzu 8100 FT-IR spectrometer by ATR and KBr method, respectively. 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°C/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 a probe current of 0.01  $\mu$ A. X-ray diffraction (XRD) analysis of the deposited metal was carried out with an X-ray diffractometer (Rigaku Denki Co. Ltd., RINT-2100), using Cu K $\alpha$  radiation at 40 kV and 14 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a photoelectron spectrometer (JEOL Ltd., JPS-90SX), using Mg K $\alpha$  radiation at 12 kV and 5 mA, after argon-ion beam etching for 10 s (depth, ca. 10 nm) at the condition of an accelerating voltage of 500 V and an ion-beam current of 50 mA, to avoid contamination of the uppermost surface of the metallized film.

## RESULTS AND DISCUSSION

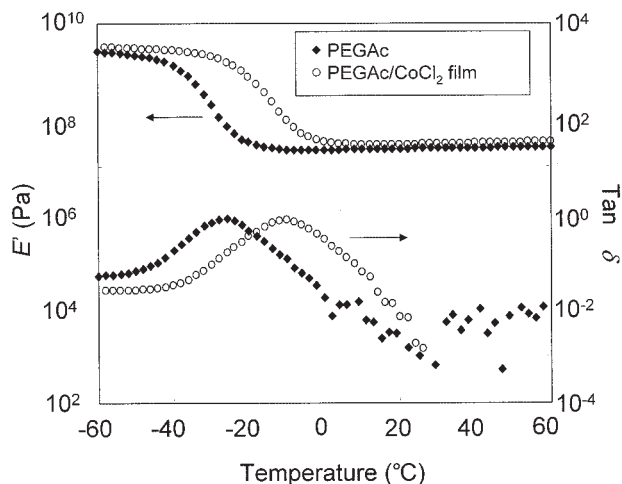
### Various properties of the crosslinked acrylate resins, containing cobalt(II)chloride

As metal chloride added to photopolymerization system of PEGAc/THFAc and Irgacure 184, cobalt(II)



**Figure 2** IR spectra at (a) PEGAc, (b) THFAC, (c) UV-cured PEGAc/CoCl<sub>2</sub> (air side), and (d) UV-cured PEGAc/THFAC (80/20)/CoCl<sub>2</sub> (air side).

chloride, nickel(II) chloride, copper(II) chloride, and iron(II) chloride were examined. Although the metal chlorides, except for the nickel chloride, were soluble in PEGAc and THFAC, the cases using the copper chloride and iron chloride did not afford fully cured resins. Consequently, the cobalt chloride gave a satisfactory result. We do not know the clear reason, but it is thought that copper chloride and iron chloride may disturb the radical polymerization initiated by photodecomposition of Irgacure 184 by the action of some redox reactions. Progress of the curing reaction of PEGAc/THFAC in the presence of cobalt(II) chloride was identified by the use of IR spectroscopy (Fig. 2). In the IR spectrum of PEGAc or THFAC, the absorption peak at 1650 cm<sup>-1</sup> is assigned to the stretching of vinyl group attached to the carbonyl group, and the peaks at 1415 and 990 cm<sup>-1</sup> correspond to =CH<sub>2</sub> group in-plane and out-of-plane bending. Their absorption peaks related to the vinyl group disappeared in the ATR FT-IR spectra of the air side of the photocured CoCl<sub>2</sub>-containing PEGAc and PEGAc/THFAC (80/20) films, indicating that the vinyl group of the acrylate resins polymerized, as is shown in Figure 1. The cor-

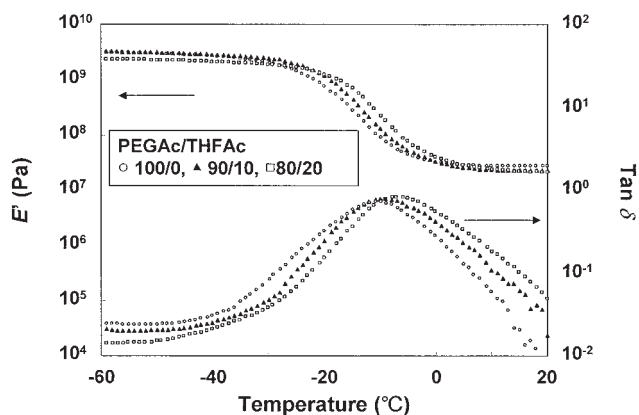


**Figure 3** Dynamic viscoelastic curves of the UV-cured PEGAc and PEGAc/CoCl<sub>2</sub> films.

responding ATR FT-IR spectra at the glass side of the CoCl<sub>2</sub>-containing cured films showed almost the similar pattern.

Figure 3 shows the dynamic viscoelastic curves of the UV-cured PEGAc and PEGAc/CoCl<sub>2</sub> films. The tan  $\delta$  peak temperature (-9.0°C) of the UV-cured PEGAc/CoCl<sub>2</sub> film was much higher than that of the UV-cured PEGAc film (-24.7°C), suggesting chelation of cobalt ion with alkyleneoxy unit of the acrylate resin. The storage modulus ( $E'$ ) of the cured PEGAc film at a glassy state around room temperature is almost the same as that of the cured PEGAc/CoCl<sub>2</sub> film, indicating that both the films have almost similar crosslinking density and that the cobalt chloride does not disturb the photocuring reaction.

Figure 4 shows the dynamic viscoelastic curves of the UV-cured PEGAc/THFAC/CoCl<sub>2</sub> films as a function of THFAC content. The tan  $\delta$  peak temperature (-10.8, -9.0, and -7.1°C) slightly rose with increasing THFAC content (0, 10, and 20 wt %), in agreement with



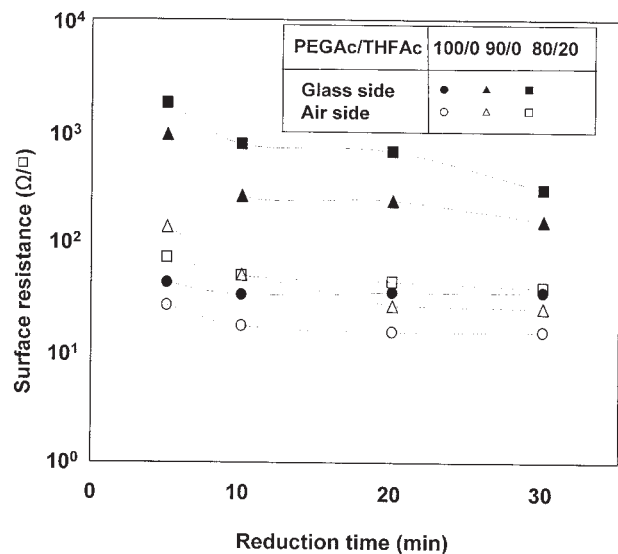
**Figure 4** Dynamic viscoelastic curves of the UV-cured PEGAc/THFAC/CoCl<sub>2</sub> films.

a higher  $T_g$  (60°C) of the UV-cured THFAC than with PEGAc. This fact should be attributed to the fact that PEGAc has a more flexible polyethyleneoxy unit. Regarding the storage modulus, the PEGAc/THFAC (100/0) film has the highest value, indicating that the increase of THFAC content causes a lowering of the crosslinking density.

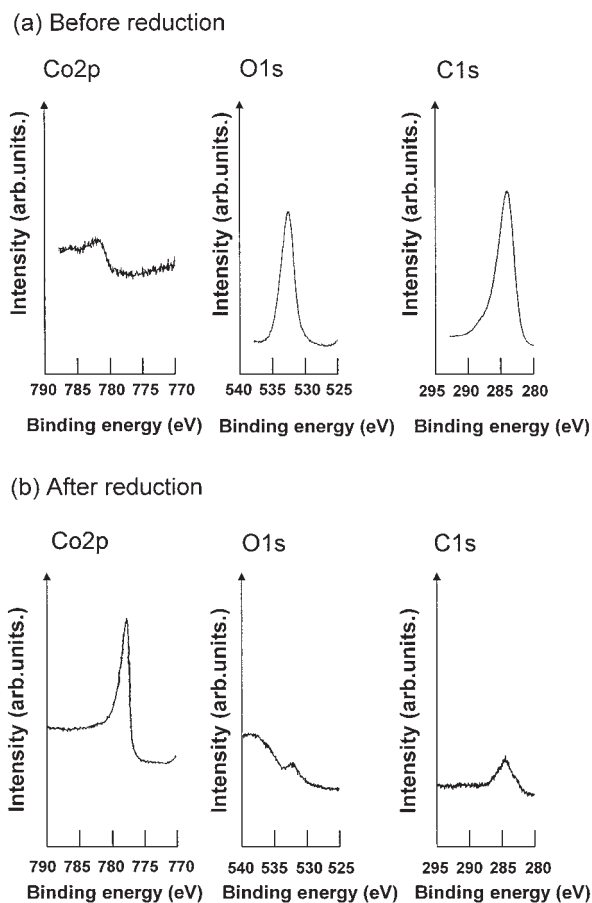
### Surface metallization of the crosslinked acrylate resins, containing cobalt(II) chloride

The reduction of the UV-cured acrylate resins, containing cobalt(II) chloride with aqueous sodium borohydride at 20°C, successfully afforded the films with metallic luster. The change of surface resistance of the metallized PEGAc/THFAC films is shown in Figure 5. The insulated film before reduction became a surface-conductive film after reduction. The surface resistance dropped with increasing reduction time until 5 min, and then became almost unchanged after 10 min, indicating that the reduction is almost completed at 10 min. The finally attained surface resistance increased with increasing THFAC content. The increase of THFAC content may hinder the migration of cobalt ion, as expected from the increase of  $T_g$ . As a whole, surface resistance at air side was lower than that at glass side. The increasing trend of surface resistance with THFAC content was more prominent at the glass side of the metallized film.

Figure 6 shows typical XPS spectra of the air side of the PEGAc/THFAC (90/10) film, before and after metallization. Before reduction, the peak at 781 eV is assigned to  $\text{Co}^{2+}$ , and intense peaks related to C 1s



**Figure 5** Relation between reduction time and surface resistance of the UV-cured PEGAc/THFAC/CoCl<sub>2</sub> films; the air side of PEGAc/THFAC: ○ 100/0, △ 90/10, □ 80/20, and the glass side of PEGAc/THFAC: ● 100/0, ▲ 90/10, ■ 80/20.



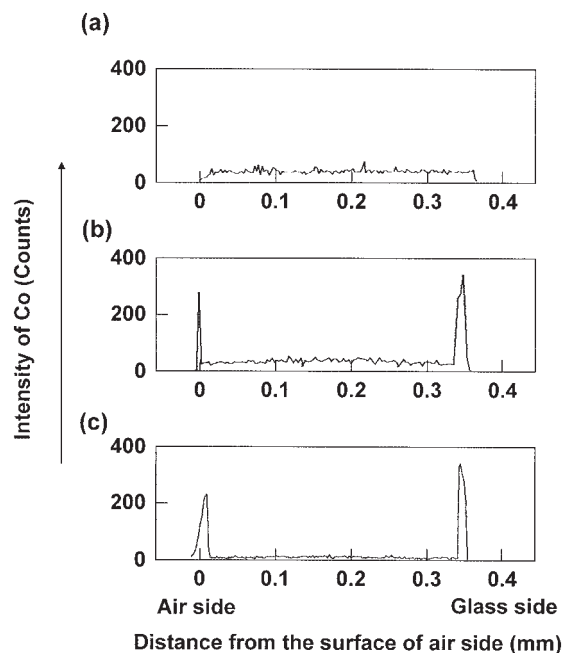
**Figure 6** XPS spectra of the Co 2p<sub>2/3</sub>, O 1s, and C 1s regions of the CoCl<sub>2</sub>-containing PEGAc/THFAC (90/10) films at the air side (a) before reduction and (b) after reduction for 30 min.

and O 1s of acrylate resin are observed. On the other hand, the intense peak at 778.5 eV 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 for the film after reduction for 30 min, indicating that the metal ion migrates to the surface, and is reduced to pure metal. The glass side surface of the metallized film and the other composition film showed almost the similar spectra.

Figure 7 shows typical change of the elemental distribution of Co in the depth direction of the PEGAc/THFAC (90/10) film (thickness, ca. 0.35 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. From the results of EPMA and XPS, it is obvious that cobalt ion migrates to the film surface and reduces to cobalt metal by the reaction with sodium tetrahydroborate solution.

Figure 8 shows the EPMA map of cobalt and carbon in the depth direction of the films before and after



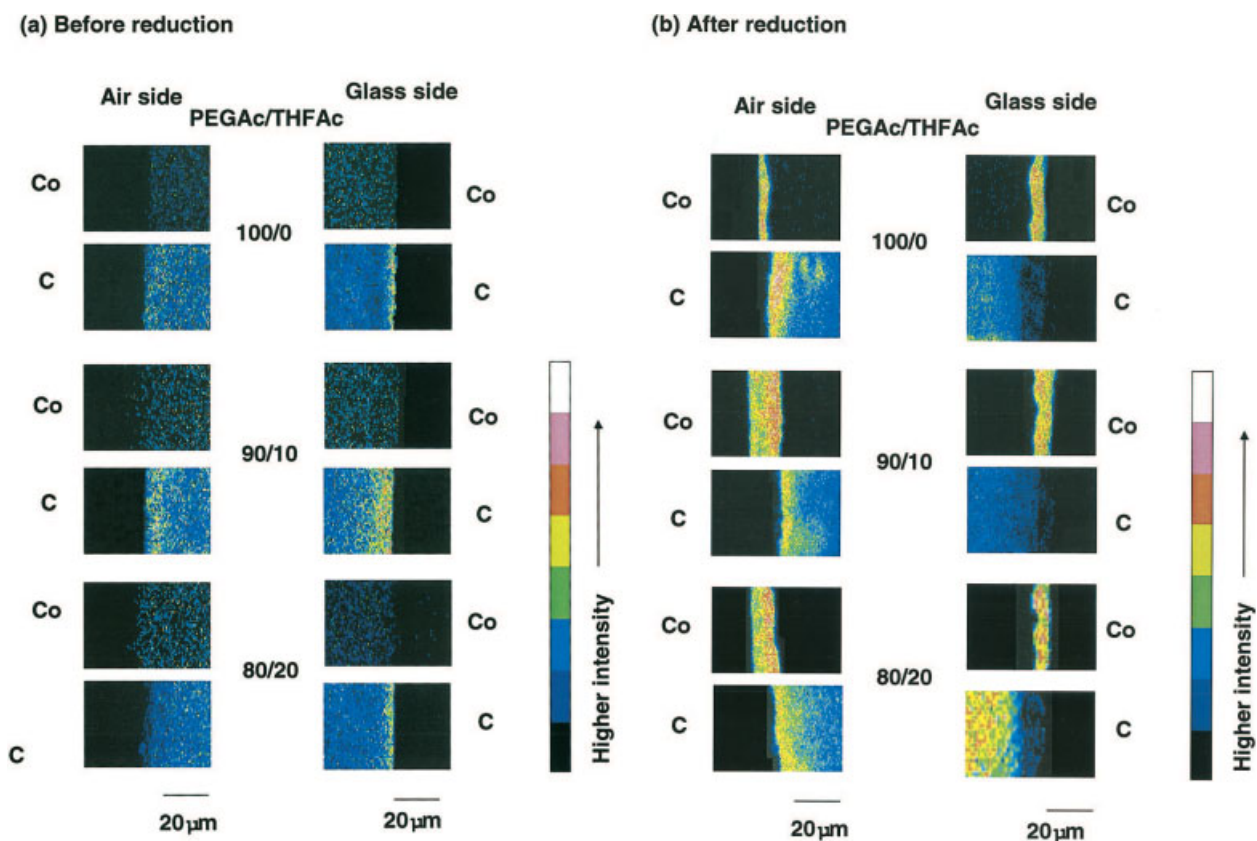


**Figure 7** Elemental distribution of Co by EPMA line analysis in the depth direction of the UV-cured PEGAc/THFAc (90/10)/CoCl<sub>2</sub> film as a function of reduction time: (a) 0 min (before reduction), (b) 5 min, and (c) 30 min.

reduction. Regarding the film before reduction, cobalt ion homogeneously distributes in the depth direction of the film, in agreement with Figure 7(a). Regarding after-reduction, it was confirmed that the cobalt metal layer and polymer layer clearly separated at the air side of all the metallized films. On the other hand, it appears that the cobalt metal layer at the glass side of the metallized film with a higher THFAc content contains more polymer component, as is obvious from the carbon map at the glass side. This result is in agreement with the trend of surface resistance at the glass side of the metallized films. Although the cause of the difference of metallization behavior at the air and glass sides is not clear, it is thought that the metal is harder to deposit out of the surface at the glass side than at the air side, because of some difference of the surface state. Also, little XRD 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.

## CONCLUSIONS

The cobalt ion incorporated in the crosslinked acrylate resins, which was prepared by the UV-curing reaction



**Figure 8** EPMA maps of cobalt and carbon in the depth direction of the CoCl<sub>2</sub>-containing PEGAc/THFAc film (a) before reduction and (b) after reduction for 30 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

of PEGAc/THFAc, smoothly migrated to both sides of the film, and then reduced to pure metal by dipping the film in aqueous  $\text{NaBH}_4$  solution, at  $25^\circ\text{C}$  for 10–30 min. The surface of the reduced film had metallic luster, and the surface resistance reached to  $15 \Omega/\text{sq}$ . The XPS and XRD analyses revealed that the generated cobalt is pure and has a low degree of crystallinity. The EPMA measurements revealed that the cobalt layer generated at the glass side of the film with a higher THFAc content contains more polymer component, in agreement with the order of surface resistance. This metallization of UV-cured acrylate resins may be applicable to some field of coating materials having electric conductivity and metallic luster.

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