Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 5617–5623

polymer

www.elsevier.com/locate/polymer

Metallization of cross-linked polyurethane resins by reduction of polymer-incorporated metal ion

Mitsuhiro Shibata*, Tsuyoshi Ito

Department of Industrial Chemistry, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan

Received 24 March 2003; received in revised form 7 July 2003; accepted 14 July 2003

Abstract

Polyurethane (PU) resins having different degree of cross-linking were prepared by the reaction of 4,4′-methylenebis(phenyl isocyanate) (MDI) with various molar ratio of two kind of pentaerythritol ethoxylates (PEE15, ratio of ethyleneoxy (EO) unit/hydroxyl (OH) unit = 15/4; PEE3, EO/OH = 3/4) in the presence of cobalt(II) chloride at 100 °C for 48 h. Metallization behavior of the $CoCl_2$-containing PU resins by reduction with aqueous sodium tetrahydroborate solution was investigated by means of infra-red (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). It was confirmed by the measurement of degree of swelling and glass transition temperature that the PU resin having a higher molar ratio of PEE15/PEE3 has a lower degree of cross-linking. When the PU films were reduced at 20 °C, the PU resins with PEE15/PEE3 = 10/0, 8/2, and 6/4 afforded the films with a metallic luster, whose surface resistance increased in this order. The formation of cobalt metal on both the sides of the PU film was revealed from the results of the XPS and EPMA measurements. The PU resin having a lower degree of cross-linking could be more easily metallized by this reduction treatment.

Keywords: Metallization; Polyurethane; Cross-linking

1. 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 [1,2]. 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 by reduction of polymer-incorporated metal ions [3–12] or polymer–metal chelates [13,14] with an aqueous solution of sodium tetrahydroborate has been developed by a few groups. This method is known to be applicable to the surface metallization of highly polar linear polymers such as polyacrylonitrile, poly(vinylidene fluoride), poly(vinyl alcohol), and polyamide. However, this method has not yet applied to the surface metallization of a cross-linked polymer network. The present study describes the surface metallization of the polyurethane (PU) resins having various degree of cross-linking by reduction of polymer-incorporated cobalt(II) chloride. Our attention is focused on the elucidation of the relationship between the metallization behavior and degree of cross-linking in this method.

2. Experimental

2.1. Materials

Pentaerythritol ethoxylates (PEE15, ratio of ethyleneoxy (EO) unit/hydroxyl (OH) unit = 15/4, M_n ca. 800; PEE3, EO/OH = 3/4, M_n ca. 270) were purchased from Aldrich Chemical Company and used without further purification. Reagent-grade 4,4′-methylenebis(phenyl isocyanate) (MDI), cobalt(II) chloride, *N*,*N*-dimethylformamide

---

* Corresponding author. Tel.: +81-47-478-0423; fax: +81-47-478-0439.
E-mail address: shibata@pf.it-chiba.ac.jp (M. Shibata).

0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0032-3861(03)00650-5

(DMF), 1,4-diazabicyclo[2.2.2]octane (TED) and sodium tetrahydroborate were used without further purification.

2.2. Sample preparation

Table 1 summarizes the feed ratio of PEE15/PEE3/MDI. The molar ratio of OH group of PEE to NCO group of MDI is 1/1. A typical procedure for PEE15/PEE3/MDI (molar ratio:6/4/20, PU4) is as follows (Scheme 1):

A DMF (15 ml) solution of PEE15 (1.32 g, 1.66 mmol), PEE3 (0.298 g, 1.10 mmol), MDI (1.38 g, 5.52 mmol), cobalt(II) chloride (0.195 g, 0.50 mmol/g-PU), and TED (4.0 mg) was poured on a polypropylene plate at room temperature, and cured at 100 °C for 48 h to give a $CoCl_2$-containing polyurethane (PU4) film with a thickness of 0.7–1.0 mm.

Metallization by reduction treatment was performed by dipping the cured films containing cobalt chloride in a 0.05 wt% aqueous sodium tetrahydroborate solution at 20–60 °C for 1–12 min, followed by washing with ethanol and subsequently with toluene and drying.

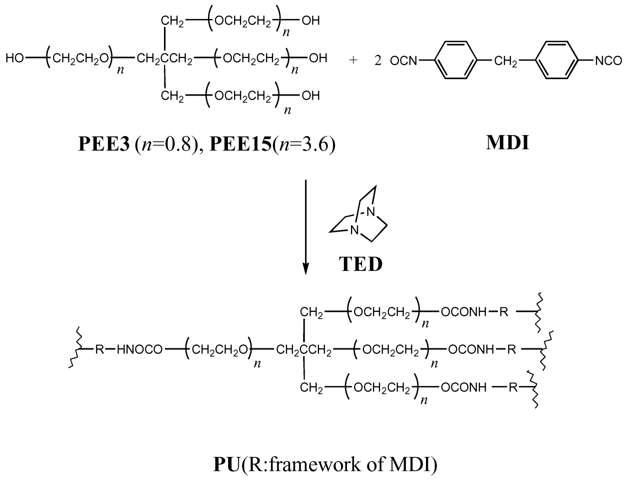
2.3. Measurements

The degree of swelling of PU resins was measured using the following equation:

$$Q = (W_a - W_b)d_p/(W_b d_s)$$

where Q is degree of swelling, W_a (g) is weight of swelled PU at the equilibrium state, W_b (g) is weight of dried PU, d_p (g/cm^3) is density of PU, and d_s (g/cm^3) is density of DMF. In order to remove the cobalt chloride, the $CoCl_2$-containing PU was dipped in DMF for several hours at room temperature, and again dipped in fresh DMF for several hours. This procedure was several times repeated until the color of cobalt chloride disappears in the solution. After that, the obtained sample was swollen by dipping in DMF at 60 °C for 24 h, and the weight (W_a) at equilibrium state was measured. Next, the swelled PU was dried at 40 °C in vacuo for 24 h, and then the weight (W_b) of the dried PU was measured. The density (d_p) was measured by floating method using aqueous sodium bromide for the dried PU.

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 films with and without cobalt chloride were measured on a Shimadzu 8100 FT-IR spectrometer by ATR method. Dynamic viscoelastic measurements of the films were performed on a Rheolograph 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 (SEM, JEOL JSM-6300, Japan Electron Co., Ltd). The elemental distrubution 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 μA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a photoelectron spectrometer (JEOL Ltd., JPS-90SX) using Mg K_α radiation at 12 kV and 5 mA, after argon ion beam etching for 5 s (depth: ca. 5 nm) in order to avoid contamination of uppermost surface of the metallized film.



Scheme 1. Formation of PU by the reaction of PEE15/PEE3 and MDI.

Table 1
Synthetic data and degree of swelling for the polyurethane

Code	Molar ratio of PEE15/PEE3/MDI	Degree of swelling
PU0	10/0/20	1.74
PU2	8/2/20	1.49
PU4	6/4/20	1.37
PU6	4/6/20	1.31
PU8	2/8/20	1.26
PU10	0/10/20	1.14

3. Results and discussion

3.1. Various properties of the cross-linked PU resins containing cobalt chloride

PEE15 and PEE3 were reacted with MDI (NCO/OH = 1.0) using TED as a curing catalyst in the presence of cobalt chloride (0.25–0.75 mmol/g-PU) at 100 °C for 48 h to give the PU resins containing cobalt chloride with various degree of cross-linking (Scheme 1). Their synthetic data and degree of swelling are summarized in Table 1. The degree of swelling with DMF decreased with decreasing molar ratio of PEE15/PEE3, indicating that degree of cross-linking increased with increasing PEE3 content.

Typical ATR FT-IR spectra of the PU of PEE15/PEE3 = 10/0 (PU0) with various $CoCl_2$ content are shown in Fig. 1. The absorption peak related to

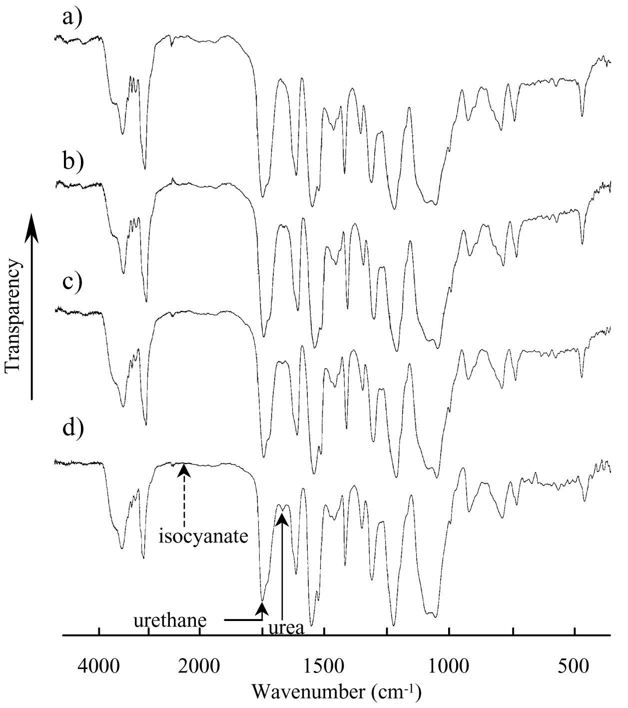


Fig. 1. IR spectra of the PU0 resins cured at 100 °C for 48 h: $CoCl_2$ content (a) 0, (b) 0.25, (c) 0.50, and (d) 0.75 mmol/g-PU.

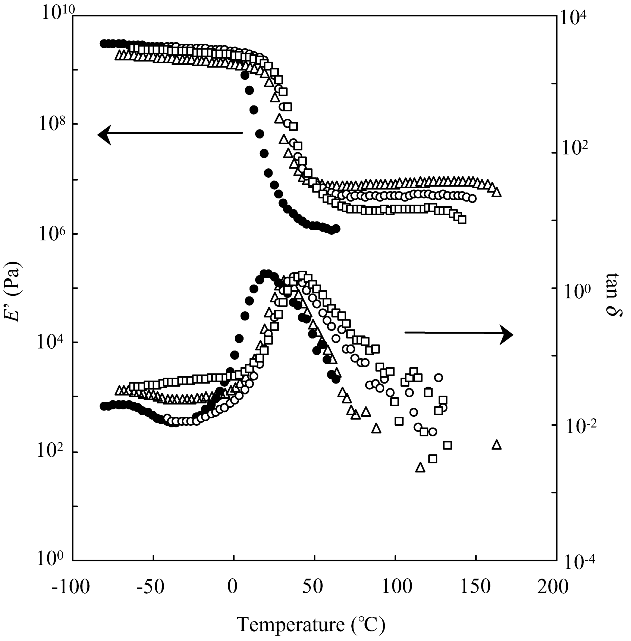


Fig. 2. Dynamic viscoelastic curves of the PU0 films with various $CoCl_2$ content: ● 0, △0.25, ○ 0.50, □ 0.75 mmol/g-PU.

isocyanate group (2270 cm^{-1}) disappeared and the peak related to C=O stretching of urethane group is observed at 1730 cm^{-1}. The peak related to C=O stretching of urea group at 1650 cm^{-1} slightly increased with $CoCl_2$ content, suggesting that the product containing urea bond is formed probably by the reaction of isocyanate group with the water contained in hygroscopic cobalt chloride. There was little difference in the ATR FT-IR spectra between air side and polypropylene plate (PP) side of the PU film. The PU films of various molar ratio of PEE15/PEE3 showed similar IR spectral pattern. Fig. 2 shows the dynamic viscoelastic curves of the PU films containing various amounts of cobalt chloride. The tan δ peak temperature (21–42 °C) corresponding to glass transition temperature (T_g) increased with $CoCl_2$ content, indicating some chelation of cobalt ion with ethyleneoxy unit of PU and/or promotion of curing reaction by the action of cobalt chloride. Also, the tan δ peak temperature (38–86 °C) of the PU resins containing 0.5 mmol/g-PU $CoCl_2$ increased with decreasing PEE15/PEE3 ratio (Fig. 3). Because T_g rises with an increase of degree of cross-linking, this is in agreement with the result of degree of swelling. Also, the storage modulus (E') decreases around 10–50 °C, and gradually becomes constant (ca. 5 MPa). This is a typical pattern of cross-linked polymer.

3.2. Surface metallization of the cross-linked PU resins containing cobalt chloride

The cross-linked PU resins containing cobalt chloride were reduced with 0.05 wt% aqueous sodium tetrahydroborate solution at 20 °C. The change of surface resistance during the reduction treatment for $CoCl_2$-containing PU0 is shown in Fig. 4. When the PU0 containing 0.5 mmol/g-PU $CoCl_2$ was reduced, the film having metallic luster on both the sides was obtained, and the air side had lower surface resistance than the PP side. Although the higher content (0.75 mmol/g-PU) of cobalt chloride results in the slight

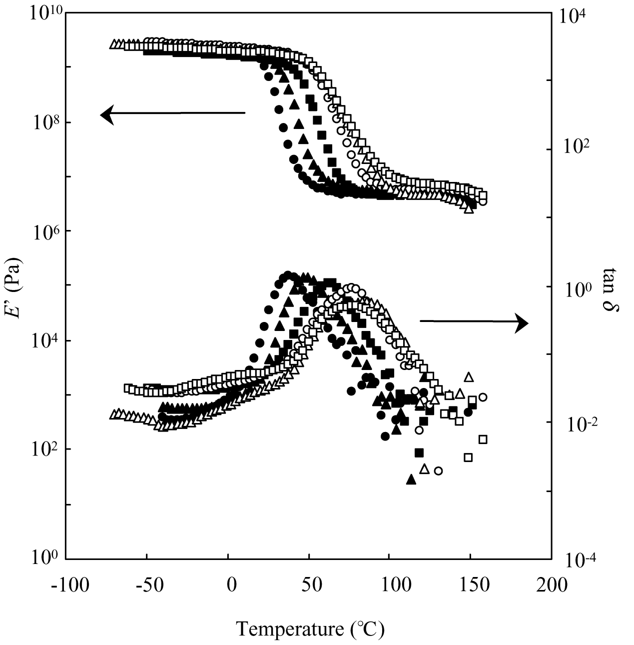


Fig. 3. Dynamic viscoelastic curves of the 0.5 mmol/g-PU $CoCl_2$-containing PU resins with various molar ratio of PEE15/PEE3: ● 10/0, ▲ 8/2, ■ 6/4, ○ 4/6, △ 2/8, □ 0/10.

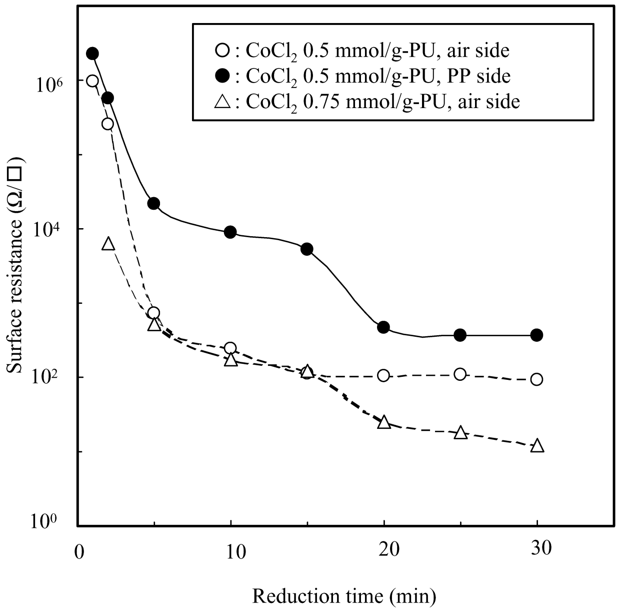


Fig. 4. Relation between reduction time and surface resistance of the PU0 resins containing cobalt chloride during the reduction with aqueous sodium tetrahydroborate at 20 °C.

decrease of surface resistance, the surface resistance was too low to be measured in case of 0.25 mmol/g-PU. The influence of PEE15/PEE3 ratio and reduction temperature on the surface resistance is shown in Fig. 5. PU0, PU2, and PU4 resins containing 0.5 mmol/g-PU $CoCl_2$ afforded the metallized film by the reduction at 20 °C, and the surface resistance decreased with reduction time, and becomes almost constant after 10 min. The finally attained surface resistance of PU4, PU2, and PU0 decreases in that order. This order is in accord with the decreasing order of degree of cross-linking. In case of PU6, PU8, and PU10 resins, no metallic luster on the film surface was appeared by the reduction at 20 °C, and the surface resistance was too low to be measured. It is thought that the migration of cobalt ion to the film surface is hindered by the cross-linked structure. When the reduction temperature is raised to 40 °C, the surface resistance for PU2 and PU4 smoothly dropped to the same level as PU0 ($10^2\ \Omega\ \square$ order) (Fig. 5). The PU6 film containing 0.5 mmol/g-PU $CoCl_2$ had some metallic luster by the reduction at 40 °C for 30 min, and the surface resistance was $2.5 \times 10^5\ \Omega\ \square$. The PU8 and PU10 resins did not metallize even at 40 °C. On the other hand, the reduction at 60 °C did not afford a successful result as a whole. For example, the surface resistance of the PU0 resin containing 0.5 mmol/g-PU $CoCl_2$ after the reduction at 60 °C for 20 min was $1.0 \times 10^4\ \Omega\ \square$. As the reduction solution became turbid and black in case of 60 °C, it is thought that the reduced cobalt migrated to the solution or that side reactions occurred.

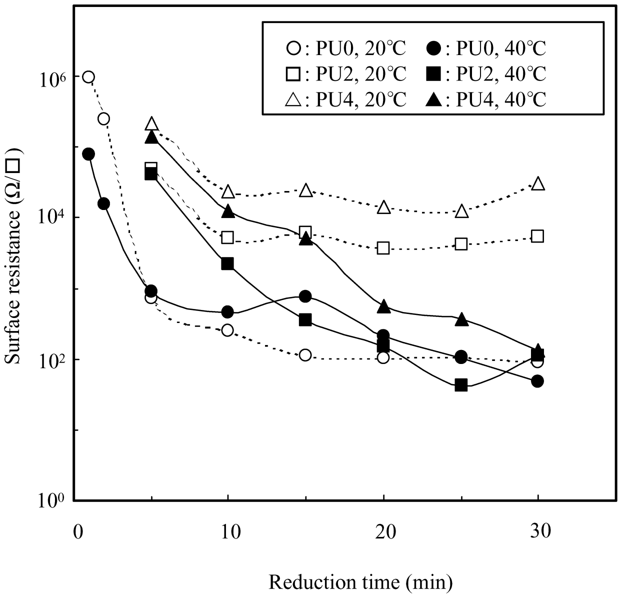


Fig. 5. Relation between reduction time and surface resistance at air side of the PU0, PU2, and PU4 containing 0.5 mmol/g-PU $CoCl_2$ during the reduction with aqueous sodium tetrahydroborate.

Fig. 6 shows XPS spectra of the metallized PU0 film. The intense peak related to the pure Co metal ($2p_{3/2}$:778.5 eV) is observed, and the peaks related to C 1s, O 1s, Cl2p, and B1s were very weak, indicating that the metal ion migrates to the surface, and is reduced to pure metal. Figs. 7 and 8 show the elemental distribution of Co and Cl in the depth direction of the PU0 film containing 0.5 mmol/g-PU $CoCl_2$ (thickness

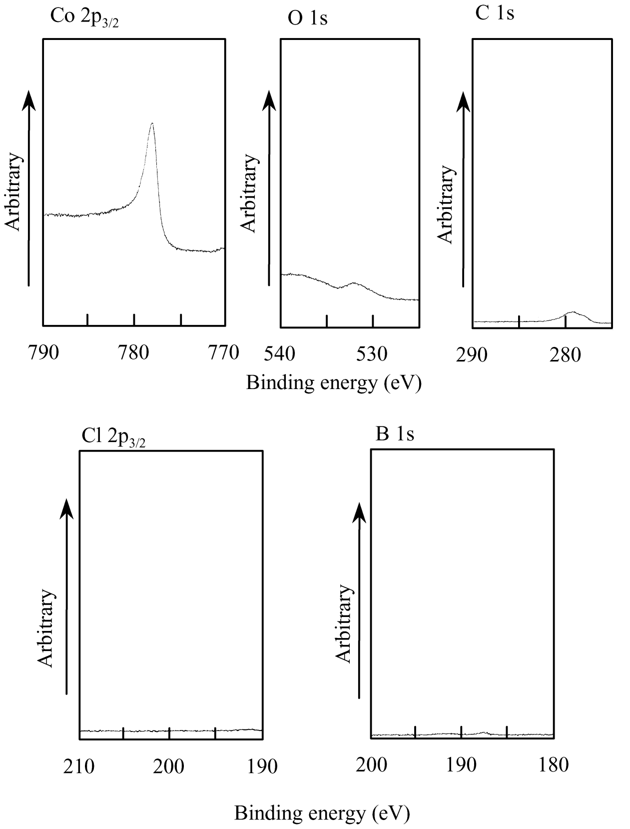


Fig. 6. XPS spectra of the Co 2p, O 1s, C 1s, Cl 2p, and B 1s regions of the metallized PU0 film: $CoCl_2$ 0.5 mmol/g-PU, reduction condition 20 °C, 10 min.

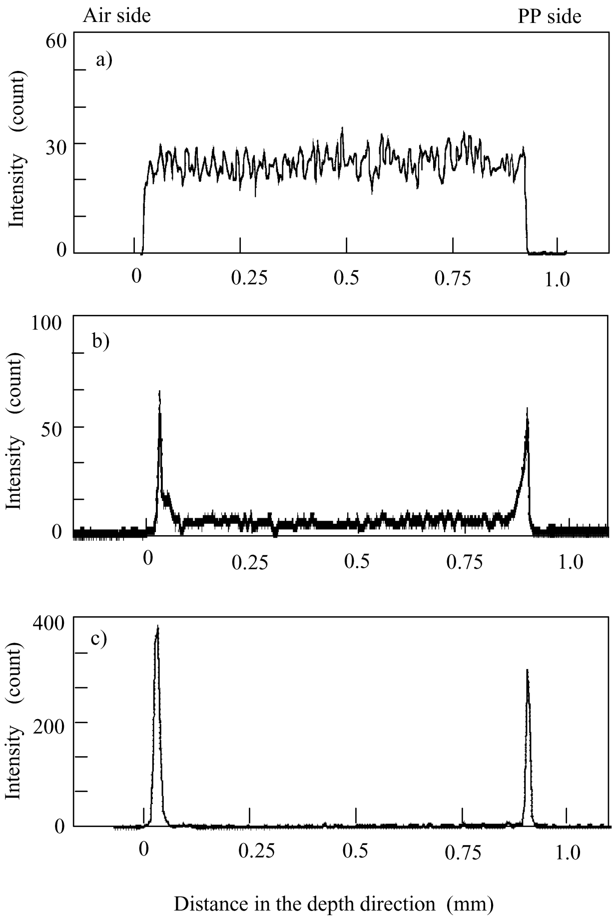


Fig. 7. Elemental distribution of Co in the depth direction of PU0 film containing 0.5 mmol/g-PU $CoCl_2$ (reduction temperature: 20 °C) as a function of reduction time: (a) 0 min (before reduction), (b) 2 min, and (c) 10 min.

ca. 0.9 mm) during the reduction obtained by EPMA line analysis, respectively. Before reduction, the cobalt ion was homogeneously distributed in the inner part of the film. The cobalt migrated to the polymer surface by the reduction treatment, finally becoming a little more densely distributed on the air side than on the PP side of the film. This result is in accord with the fact that the surface resistance of the air side is a little lower than that of the PP side (Fig. 4). On the other hand, chlorine migrated to the film surface at 2 min, and almost disappeared in the film at 10 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 chlorine ion finally passed in the reduction solution. For the 0.5 mmol/g-PU $CoCl_2$-containing PU10 resin, it was also confirmed by EPMA measurement that the cobalt and chlorine ions did not migrate to the film surface because of the high cross-linking density. Fig. 9 shows the comparison of cobalt atom distribution after the reduction at 20 °C for 10 min for the PU films with various PEE15/PEE3 molar ratios. It is obvious that the migration of cobalt is more hindered with increasing cross-linking density. For PU8 and PU10 resins, no migration of cobalt to the film surface occurred. This result was also supported from the SEM photographs of the metallized film surface. As is obvious from Fig. 10, the particles of cobalt metal are observed for the metallized PU0, PU2, and PU4 resins. Especially for PU0, relatively large metal particles are densely deposited on the surface. The generated metal particles are not continuous. A relatively high surface resistance of the metallized film may be related to the rough surface of the formed metal. On the other hand, in case of PU6, PU8, and PU10 resins, the particles of cobalt metal were not appeared.

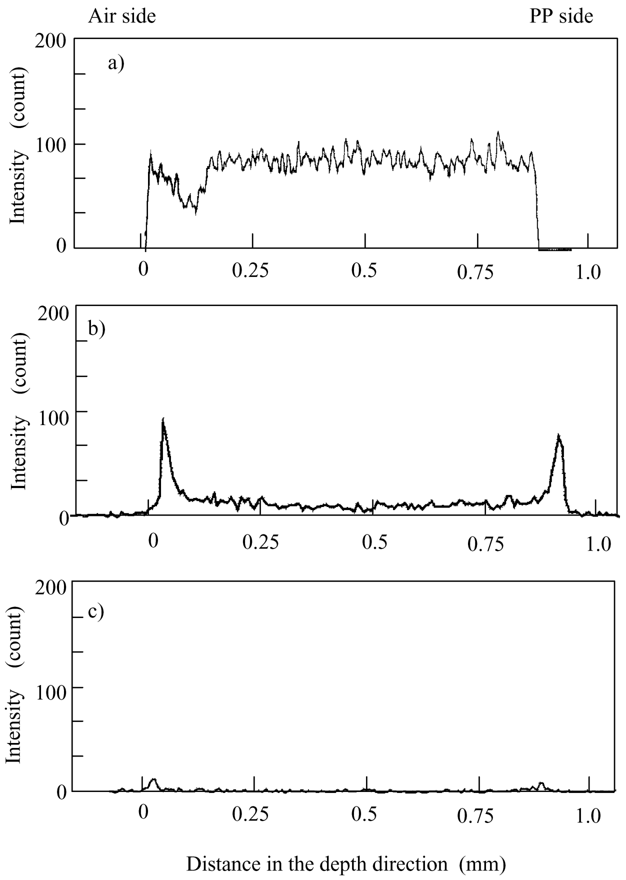


Fig. 8. Elemental distribution of Cl in the depth direction of PU0 film containing 0.5 mmol/g-PU $CoCl_2$ (reduction temperature: 20 °C) as a function of reduction time: (a) 0 min (before reduction), (b) 10 min, and (c) 10 min.

The reduction of cobalt chloride by sodium tetrahydroborate in this metallization method is thought to take place near the interface between the PU film and reduction solution by a reduction mechanism similar to that of electroless plating as generally described below:

$$M^{n+} + ne \rightarrow M$$

$$\mathrm{Red} \rightarrow \mathrm{Ox} + ne$$

Because various oxidized species (Ox), for example BO_2^-, $B(OH)_3$, and $B(OH)_4^-$ toward the reduced species (Red:BH_4^-) are proposed for the electroless plating using tetrahydroborates and metal chlorides and this redox

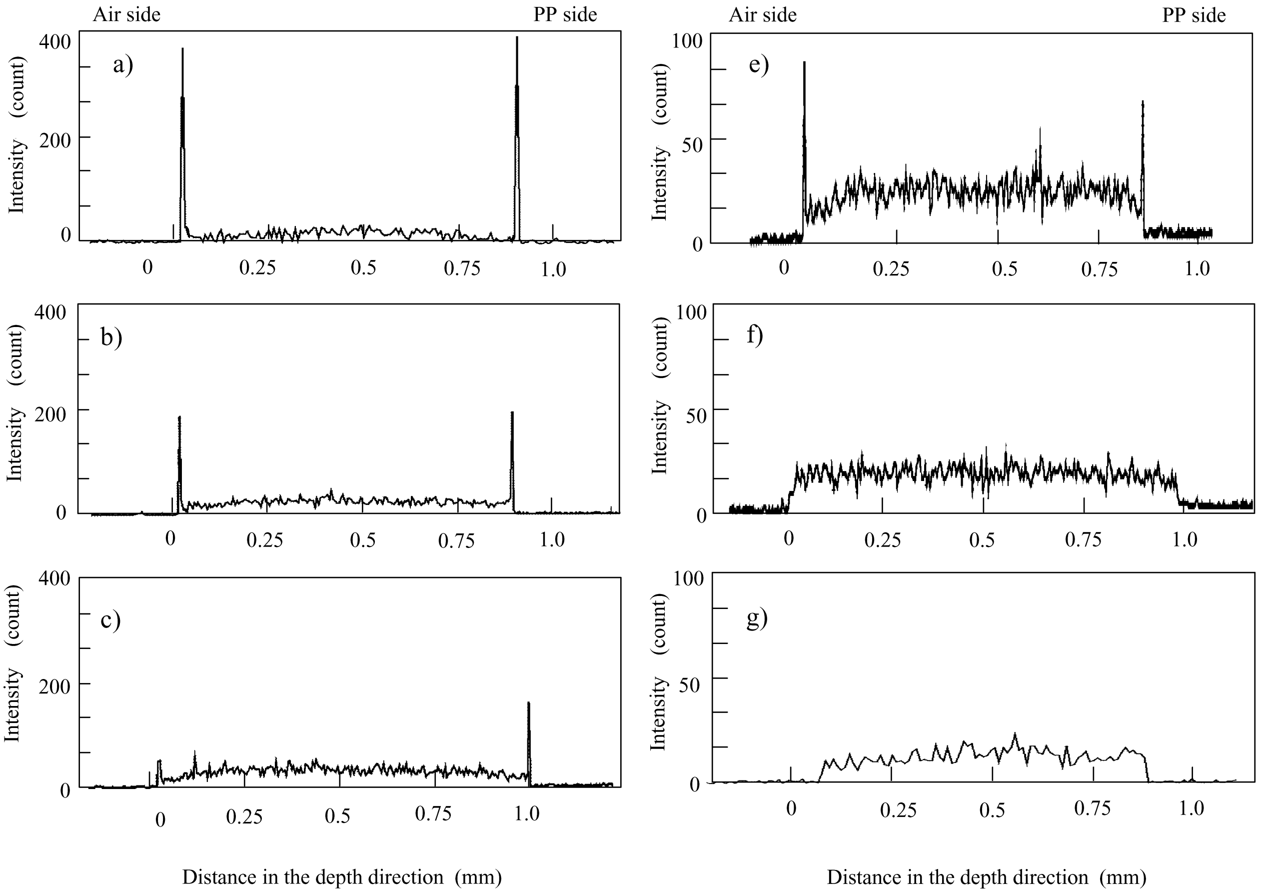


Fig. 9. Elemental distribution of Co in the depth direction of the 0.5 mmol/g-PU $CoCl_2$-containing PU films after the reduction at 20 °C for 10 min: (a) PU0, (b) PU2, (c) PU4, (d) PU6, (e) PU8, and (f) PU10.

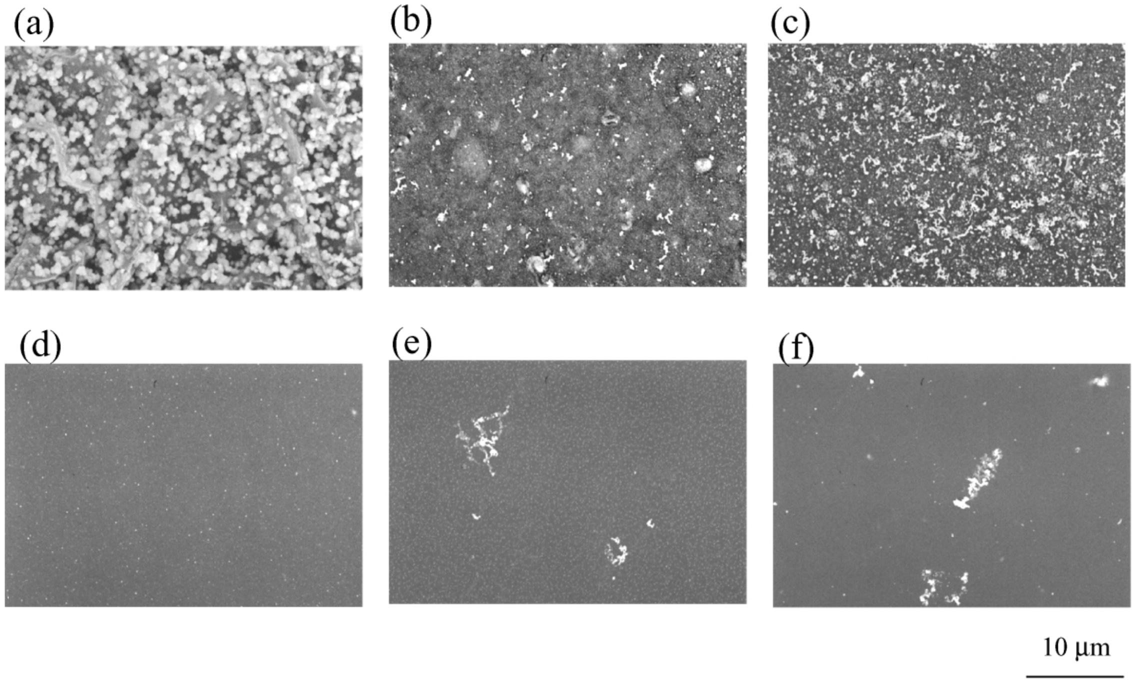


Fig. 10. SEM photographs of the surface at air side of the metallized PU films ($CoCl_2$ 0.5 mmol/g-PU, reduction condition 20 °C, 10 min): (a) PU0, (b) PU2, (c) PU4, (d) PU6, (e) PU8, and (f) PU10.

reaction is very sensitive to p*H* of the reduction solution [15–17], we cannot confine the redox reaction equation at present. The migration of cobalt ion to the film surface before reduction is thought to be caused by at least diffusion of the metal chloride toward the aqueous solution. The contribution of the migration of metal ion by the formation of local electrochemical cells in the solid polymer electrolyte is now under investigation.

4. Conclusions

The $CoCl_2$-containing PU resins with different degrees of cross-linking were prepared by the reaction of various molar ratio of PEE15/PEE3/MDI in the presence of cobalt(II) chloride at 100 °C for 48 h. The PU resin having a lower molar ratio of PEE15/PEE3 showed a lower degree of swelling and a higher glass transition temperature, indicating the formation of a higher degree of cross-linking. When the PU films were reduced at 20 °C, the PU resins with PEE15/PEE3 = 10/0, 8/2, and 6/4 afforded the films with a metallic luster, whose surface resistance increased in this order. In case of the PU resins with PEE15/PEE3 = 4/6, 2/8 and 0/10, the films did not metallize. The PU resin having a lower degree of cross-linking can be more easily metallized by this reduction treatment. The XPS analysis revealed that the generated cobalt is pure metal. This novel metallization method of network polymer may be applicable to some field of electronic and/or magnetic materials.

Acknowledgements

The authors wish to thank Dr R. Yosomiya for the helpful suggestions.

References

[1] Mittal KL, Susko JR. Metallized plastics 1: fundamental and applied aspects. New York: Plenum Press; 1989.
[2] Mallory GO, Hajdu JB. Electroless plating:fundamentals and applications. American Electroplaters and Surface Finishers Society, Orland: William Andrew Inc; 1990.
[3] Yosomiya R, Hirata M, Morimoto K, Marutuka T. Japan Patent 274778; 1988.
[4] Yosomiya T, Ono H, Yosomiya R. Angew Makromol Chem 1992; 197:49–58.
[5] Yosomiya T, Sato Y, Yosomiya R. Angew Makromol Chem 1993; 206:209–16.
[6] Shibata M, Yosomiya R, Yosomiya T. Angew Makromol Chem 1997; 253:183–91.
[7] Haga Y, An H, Sato Y, Yosomiya R, Yosomiya T. In: Mittal KL, editor. Plastics: fundamentals and applications. New York: Marcel Dekker Inc; 1998. p. 85–93.
[8] Shibata M, Beniya H, Yosomiya R, Yosomiya T. J Polym Res 2000; 7(1):57–61.
[9] Yen CC, Chang TC, Kakinoki H. J Appl Polym Sci 1990;40:53–66.
[10] Yen CC, Huang CJ, Chang TC. J Appl Polym Sci 1991;42:439–51.
[11] Huang CJ, Yen CC, Chang TC. J Appl Polym Sci 1991;42:2237–45.
[12] Huang CJ, Yen CC, Chang TC. J Appl Polym Sci 1991;42:2267–77.
[13] Nakamae K, Mohamed NA. Polymer 1993;34(18):3940–7.
[14] Mohamed NA, Nakamae K. In: Mittal KL, editor. Metallized plastics:fundamentals and applications. New york: Marcel Dekker Inc; 1998. p. 27–44.
[15] Sullivan EA. US Patent 2,942,990; 1960.
[16] Narcus H. Plating 1967;54(4):380–1.
[17] Gorbunova KM, Ivanov MV, Moiseev VP. J Electrochem Soc 1973; 120:613–5.