Deposition of Copper Sulfide on the Surface of Poly(ethylene terephthalate) and Poly(vinyl alcohol) Films in the Aqueous Solution To Give Electrically Conductive Films

Takakazu Yamamoto,* Kuniaki Tanaka, Etsuo Kubota, and Kohtaro Osakada

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received May 5, 1993. Revised Manuscript Received July 6, 1993®

Heating an aqueous solution containing $CuSO_4$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) at 60 and 70 °C causes precipitation of copper sulfide (Cu_xS) as a dark brown or black solid. Elemental analyses and XPS measurement show that the x value in the product varies from 1.7 to 1.0 depending on the preparation conditions. Similar reaction of $CuSO_4$ and $Na_2S_2O_3$ in the presence of poly(ethylene terephthalate) (PET) films pretreated with a methanol solution of poly(ethyleneimine) (PEI) gives copper sulfide coated PET films (Cu_xS-PET) which show the surface resistivity of 20–1000 Ω/square depending on the reaction conditions. Scanning electron micrographs of the Cu_xS–PET film show that surface of the PET films is coated with the copper sulfide layer with ca. 400-nm thickness. The PET films whose surface is coated with poly(urethane) and those pretreated with silicon-containing compounds such as (γ-aminopropyl)triethoxysilane and {γ-[*N*-(β-aminoethyl)amino]propyl}trimethoxysilane are also converted to the electrically conductive Cu_xS-PET films by immersing them at 60–70 °C in an aqueous solution of $CuSO_4$ and $Na_2S_2O_3$. Exposure of the $Cu_{1.7}S$–PET film to H_2S atmosphere causes decrease in the surface resistivity from 80 Ω/square to 15 Ω/square accompanied by change of the color of the film from brown to green. Poly(vinyl alcohol) (PVA) and poly(2-cyano-1,3-phenylene oxide) (ID-300) films also undergo deposition of Cu_xS on the surface by immersing them in the aqueous solution containing copper sulfides to give electrically conducting films.

Introduction

Electrically conductive films composed of organic polymers have potential utility as the materials for the electrical and optical devices since many organic polymers have high elasticity and transparency. Dispersion of fine particles of electrically conductive inorganic materials such as metal and graphite carbon[1,2] in polymer matrices is a useful method to obtain the films which have both electrical conductivity and elasticity. Recently we have reported preparation of the electrically conductive polymer films containing fine particles (10–200 nm in the diameter) of metal sulfides such as CuS, CdS, ZnS, and HgS[3] by adding organic polymers such as poly(acrylonitrile) and poly(vinyl alcohol) to the organosols of metal sulfides in DMF (*N*,*N*-dimethylformamide) or DMSO (dimethyl sulfoxide) followed by casting the reaction mixture on glass plates.[4] The films have proved to be useful as electric devices or shielding materials for electromagnetic wave.

Deposition of the metal sulfide fine particles on the surface of organic polymer films is another promising approach to obtain electrically conductive films. Although this method has the advantage of giving the electrically conductive films with relatively large size, there have been only a few reports[5] on the subject probably due to difficulty in obtaining stable contact between inorganic compound layer and the polymer film surface and also due to unsuitableness of the polymer film as the substrate of electrodeposition or vacuum deposition of the metal sulfides.

Here we report preparation of the electrically conductive Cu_xS–PET films (PET = poly(ethylene terephthalate)) by deposition of copper sulfide in the aqueous solution on the PET film surface. Characterization and the electrical properties of the films are also described.

Experimental Section

Materials and Measurement. $CuSO_4 \cdot 5H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, H_3PO_4, MeCOOH, MeCOONa, and NaOH were purchased and used without further purification. PET film (50-μm thickness)

* Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) (a) Miyasaka, K.; Watanabe, K.; Jojima, E.; Aida, H.; Sumita, M.; Ishikawa, K. *J. Mater. Sci.* **1982**, *17*, 1610. (b) Shimizu, Y.; Tanemura, M.; Sumita, M.; Miyadera, N.; Miyasaka, K. *Sen-i Gakkaishi* **1986**, *42*, T-261. (c) Sumita, M.; Asai, S.; Miyadera, N.; Jojima, E.; Miyasaka, K. *Colloid Polym. Sci.* **1986**, *264*, 212.

(2) Grue, B. E.; Schenfil, E. Z. *Electrically Conductive Polymer Composite*; Chimia: Moscow, 1984.

(3) (a) Yamamoto, T.; Taniguchi, A.; Kubota, K.; Tominaga, Y. *Inorg. Chim. Acta* **1985**, *104*, L1. (b) Dev, S.; Taniguchi, A.; Yamamoto, T.; Kubota, K.; Tominaga, Y. *Colloid Polym. Sci.* **1987**, *265*, 922. (c) Yamamoto, T.; Taniguchi, A.; Dev, S.; Kubota, E.; Osakada, K.; Kubota, K. *Colloid Polym. Sci.* **1991**, *269*, 969. (d) Yamamoto, T. *Jpn. Kokai* **1986**, 61-91005. (e) Osakada, K.; Taniguchi, A.; Kubota, E.; Dev, S.; Tanaka, K.; Kubota, K.; Yamamoto, T. *Chem. Mater.* **1992**, *4*, 562.

(4) (a) Yamamoto, T.; Kubota, E.; Taniguchi, A.; Kubota, K.; Tominaga, Y. *J. Mater. Sci. Lett.* **1986**, *5*, 132. (b) Kubota, E.; Yamamoto, T. *Jpn. J. Appl. Phys.*, **1987**, *26*, L1601. (c) Yamamoto, T.; Kubota, E. *Colloid Polym. Sci.* **1989**, *267*, 546. (d) Yamamoto, T.; Kubota, E.; Taniguchi, A.; Dev, S.; Tanaka, K.; Osakada, K.; Sumita, M. *Chem. Mater.* **1992**, *4*, 570.

(5) (a) Kang, E. Y.; Chung, E. J.; Im, S. S. *J. Appl. Polym. Sci.* **1987**, *33*, 317. (b) Yanagida, S.; Enokida, T.; Shindo, A.; Shiragami, T.; Ogata, T.; Fukumi, T.; Sakagami, T.; Mori, H.; Sakata, T. *Chem. Lett.* **1990**, 1773.

0897-4756/93/2805-1352$04.00/0

by Teijin Co., PET film precoated with poly(urethane) (100-μm thickness) by Diafoil Co., biaxially oriented poly(vinyl alcohol) (PVA) film (Bovlon no. 250, 99.9% hydrolyzed; M_n = 1700, 25-μm thickness) by Nichigo Film Co., and poly(2-cyano-1,3-phenylene oxide) (ID-300) by Idemitsu Kosan Co. were used as received. Poly(ethyleneimine) (PEI, M_n = 1000) was used as the methanol solution.

Electrical conductivity was measured by a Mitsubishi Yuka AP-MCP-T400 electrometer. Elemental analyses were carried out by Dr. Masako Tanaka and Mr. Toyoharu Saito in our laboratory using Yanagimoto CHN autocorder and Yazawa Halogen and sulfur analyzer. UV–vis spectra were measured on Hitachi 200–20 or JASCO Ubest-35 UV/vis spectrophotometers.

Preparation of Copper Sulfide Deposited PET Film. A typical experimental procedure is as follows. A PET film (1 cm × 2 cm) was immersed for 48 h at room temperature in a methanol solution (1%) of PEI (ca. 200 mL) in a 300-mL beaker and dried in the air for 2–3 h. The PEI-treated film was connected with a wire and dipped in an aqueous solution (100 mL) of $CuSO_4 \cdot 5H_2O$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) in a beaker. The reaction mixture was heated at 70 °C by an oil bath with magnetic stirring. Color of the solution changed from yellow green to yellow brown, then dark brown, and finally to black in the initial 0.5 h. A small amount of black solid was deposited, and the film was colored yellow. Heating the reaction mixture for additional 1.5 h caused complete deposition of a black solid to give almost colorless solution. The film color was turned into green. The film was rinsed with water several times, dipped in water under ultrasonification for 0.5 h and dried in the air. The resulting Cu_xS–PET film shows surface resistivity of 55 Ω/square.

Preparation of the Cu_xS–polymer films under the other conditions was carried out analogously.

Results

Reaction of $CuSO_4$ with $Na_2S_2O_3$ To Give Copper Sulfides. Heating an aqueous solution containing equimolar mixture of $CuSO_4$ and $Na_2S_2O_3$ at 60 °C causes the immediate color change of the solution from yellow-green to brown, then to dark brown, and finally to black. The reaction for 0.5 h at the temperature causes deposition of copper sulfide as a dark brown solid. The reaction at 70 °C for 2 h causes similar intermediate color change of the mixture to give copper sulfide as black fine powders. The resulting solution of the former reaction shows blue color, while the latter reaction gives a colorless solution. The reaction at 70 °C for 2 h using 0.1 M $CuSO_4$ and 0.1 M $Na_2S_2O_3$ solution causes change of the pH value of the solution from 4.0 to 2.0. Table I shows results of elemental analyses of the formed copper sulfide prepared under several reaction conditions. The product from the reaction at 70 °C for 2 h shows the analytical values which agree with the formula of CuS, while the product from the reaction at 60 °C for 0.5 h shows analytical results indicating the formula of $Cu_{1.7}S$. The reactions at 60 °C for 2 h and at 70 °C for 0.5 h give the products with the intermediate Cu to S ratios. X-ray diffraction pattern of the product from the reaction at 60 °C for 0.5 h agrees with the authentic data of Cu_xS ($1.86 < x < 1.96$)[6a] and the product from the reaction at 70 °C for 2 h shows the diffraction pattern which is identical with that of CuS.[6b] All the results indicate that the reaction at 70 °C for 2 h gives CuS, while the reaction at 60 °C for 0.5 h gives a mixture of copper sulfides containing Cu_2S as a main component.

Deposition of Copper Sulfide on the PET Film Pretreated with PEI. Immersing the PET film already treated with a methanol solution (1%) of PEI into a solution of $CuSO_4$ and $Na_2S_2O_3$ at 60–70 °C causes deposition of dark brown copper sulfide on the film surface.

Table I. Results of Analyses of the Cu_xS and Properties of the Cu_xS–PET Film

		Cu_xS–PET film[b]		
Cu_xS deposition conditions[a]	Cu_xS analyses	color	XPS data of the film surface[c]	surface resistivity[d] (Ω/square)
60 °C, 0.5 h	$Cu_{1.7}S$	brown	Cu_2S	105 (60)
70 °C, 0.5 h	$Cu_{1.4}S$	yellow		108 (64)
60 °C, 2 h	$Cu_{1.3}S$	yellow-green		121 (38)
70 °C, 2 h	$Cu_{1.0}S$	green	CuS	55 (20)

[a] Temperature and time of immersing the film in aqueous solution of $CuSO_4$ (0.1 M) and $Na_2S_2O_3$ (0.1 M) with the initial pH of 4.0. [b] The Cu_xS–PET films were prepared by deposition of Cu_xS at pH = 4 on the PEI-pretreated PET film. [c] S2p energy region. See Figure 2. [d] Resistivity values of Cu_xS–PET film prepared from poly(urethane)-coated PET film are in parentheses.

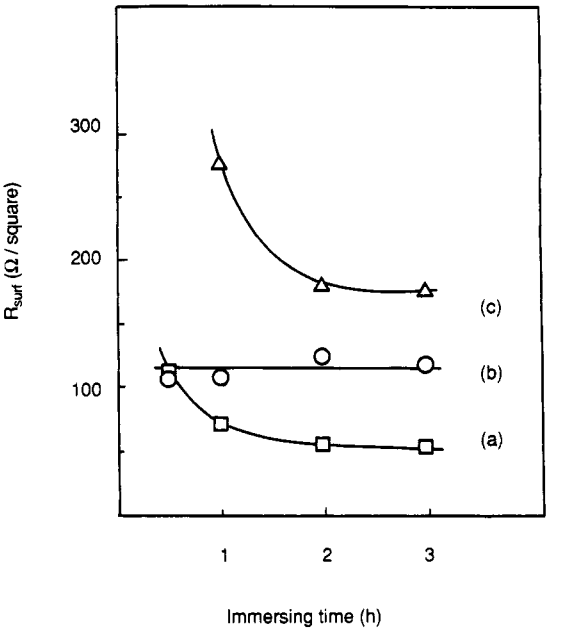


Figure 1. Change of surface resistivity (R_{surf}) of the PET films during immersion in the aqueous solutions of $CuSO_4$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) at (a) 70 °C, (b) 60 °C, and (c) 50 °C. The PET films were pretreated with a methanol solution of PEI for 48 h before deposition of Cu_xS.

Table I shows the color and the surface resistivity of the films obtained from the reactions under various conditions. The color of the Cu_xS–PET films varies from dark brown to green depending on the reaction conditions. The brown film obtained by immersing the PEI pretreated PET film in the solution of $CuSO_4$ and $Na_2S_2O_3$ at 60 °C for 0.5 h shows the surface resistivity of 105 Ω/square, while the green film obtained by the immersing at 70 °C for 2 h shows the surface resistivity of 55 Ω/square. The Cu_xS–PET film prepared from poly(urethane) coated PET film under similar conditions show lower surface resistivity of 60 Ω/square (60 °C, 0.5 h) and 20 Ω/square (70 °C, 2 h), respectively. The surface resistivity of the former film does not change for 10 months, while that of the latter film increases by 10 Ω/square in the same period.

Figure 1 shows change of the surface resistivity of the films during the immersion in the aqueous solutions of $CuSO_4$ and $Na_2S_2O_3$. The surface resistivity of the films decreases during the initial 2 h of immersing at 50 and 70 °C to reach 200 and 55 Ω/square, respectively. After 0.5 h immersing at 60 °C the PET film shows the surface resistivity of 110 Ω/square which does not change during further immersing in the solution at the temperature. The

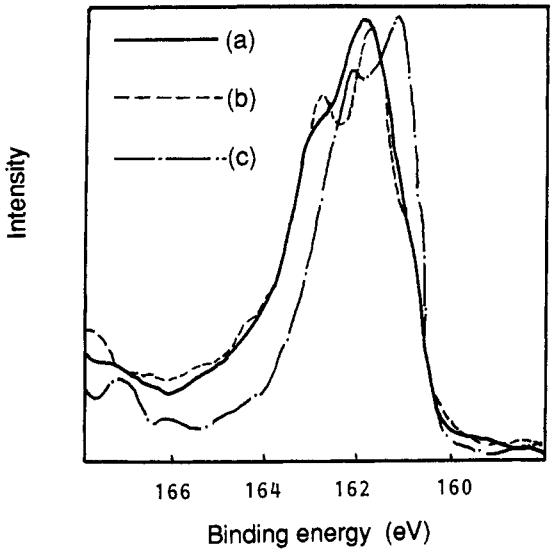


Figure 2. XPS spectra (S2p region) of (a) Cu_xS–PET film prepared by immersing PET film in the aqueous solution of $CuSO_4$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) at 70 °C for 2 h, (b) authentic CuS, and (c) Cu_xS–PET film prepared by immersing PET film in the Cu_xS solution ($[CuSO_4] = [Na_2S_2O_3] = 0.10$ M) at 60 °C for 0.5 h. The PET films were pretreated with a methanol solution of PEI for 48 h before deposition of Cu_xS.

surface resistivity of the films after immersing in the copper sulfide solution for 3 h decreases on increasing the reaction temperature from 50 to 70 °C.

Figure 2 shows the XPS spectra of S2p electrons of the Cu_xS–PET films. The spectrum of the film prepared by immersing the PET film in a solution of $CuSO_4$ and $Na_2S_2O_3$ at 70 °C for 2 h (Figure 2a) shows a peak at 161.8 eV and a shoulder peak near 163 eV. The peak positions agree with those of the spectrum of the authentic CuS (Figure 2b). The spectrum of the Cu_xS–PET film prepared by immersing the PET film at 60 °C for 0.5 h (Figure 2c) shows the peaks at 161.2 and 162.3 eV which are shifted to lower energy positions from that of CuS.

Figure 3 shows the scanning electron micrographs of the Cu_xS–PET films for both of the surface and of the cross section. The surface of the PET films immersed in the solution of $CuSO_4$ and $Na_2S_2O_3$ at 60 °C for 0.5 h is coated with the particles of copper sulfide with 200–400-nm diameters as observed in Figure 3a. Figure 3b shows that the thickness of the Cu_xS layer is ca. 400 nm. Figure 3c,d shows the scanning electron micrographs of the Cu_xS–PET film prepared by immersion of the PET film at 70 °C for 2 h. The copper sulfide particles, which have smaller size than the Cu_xS in Figure 3a, form the Cu_xS layer on the film surface with constant thickness of 400 nm.

As shown above the composition and the properties of the copper sulfide layer deposited on the PET film vary depending on time and temperature of the immersing in the solution of $CuSO_4$ and $Na_2S_2O_3$. The electrical conductivity of the Cu_xS–PET film is influenced also by pH of the solution as well as by concentration and molar ratio of $CuSO_4$ and $Na_2S_2O_3$. The conditions for preparation of highly conducting Cu_xS–PET films (<200 Ω/square) are at a pH of 2–5 and with 0.25 mM of total concentrations of $CuSO_4$ and $Na_2S_2O_3$. The Cu_xS-PET films have moderate transparency. UV–vis measurement of the films shows that the films have high transmittance (>80%) in the visible region up to 500 nm. Although the transparency decreases on increasing the wave number the minimum transmittance is 25–50% (600–700 nm) depending on the condition of Cu_xS deposition of the film.

Effect of PEI Pretreatment of the PET Film on the Properties of the Cu_xS–PET Film. As shown above, the PET films pretreated with a methanol solution of PEI is the suitable substrate for deposition of copper sulfide in the aqueous solution. The concentration of PEI in methanol used in the pretreatment in the range 0.1–5.0 wt % does not influence the surface resistivity of the Cu_xS–PET films. PET film without the PEI treatment and the film pretreated with methanol for 48 h do no give electrical conductive film due to no or poor amount of Cu_xS deposition on the film surface.

Use of poly(urethane)-precoated PET in the deposition of copper sulfide leads improvement of the surface resistivity of the obtained Cu_xS–PET film and shortening of the treatment time with PEI. Figure 4 shows change of the surface resistivity of the Cu_xS–PET films prepared by immersion of the poly(urethane) coated PET film in the solution of $CuSO_4$ and $Na_2S_2O_3$ at 60 and 70 °C. The film having surface resistivity as low as 20 Ω/square is obtained. Figure 5 shows effect of the time of pretreatment with PEI of both with and without the poly(urethane) coating of the PET film. The poly(urethane)-coated PET film is converted to the electrically conducting film (70 Ω/square) after the treatment with PEI for 0.5 h and immersing in the solution of $CuSO_4$ and $Na_2S_2O_3$ at 60 °C, while the film without precoating requires 41 h treatment with PEI to obtain surface resistivity of 200 Ω/square after immersing in the same solution.

Deposition of Copper Sulfide on the PET Films Pretreated with the Silicon-Containing Compounds. The PET films pretreated with several silicon-containing compounds are also converted to electrically conducting Cu_xS–PET films by deposition of copper sulfide on the surface. The pretreatment was carried out by immersing the films in an aqueous or methanol solution of the silicon compounds. The pretreated films do not require further treatment with PEI before deposition of Cu_xS. Table II summarizes formation of Cu_xS layer on the film surface as well as the surface resistivity of the Cu_xS–PET films. Immersing the PET film in aqueous and methanol solution of (γ-aminopropyl)triethoxysilane gives a good substrate for deposition of Cu_xS by immersing it in the solution of $CuSO_4$ and $Na_2S_2O_3$. A methanol solution of {γ-[*N*-(β-aminoethyl)]aminopropyl}trimethoxysilane and an aqueous solution of (γ-methacryloylpropyl)trimethoxysilane are effective in precoating of the PET film before deposition of Cu_xS. The other silicon-containing compounds are not useful in the precoating of the PET film.

Exposure of the Cu_xS–PET Film to H_2S To Improve the Film Properties. Exposure of the Cu_xS–PET film to H_2S causes improvement in the electrical conductivity of the film. The film prepared by immersion of the poly(urethane)-precoated PET film in the solution of $CuSO_4$ and $Na_2S_2O_3$ at 60 °C for 0.5 h shows the decrease in the surface resistivity from 80 Ω/square to 15 Ω/square on exposure to H_2S (0.1 atm) at 100 °C for 6 h, while the film prepared by immersing at 80 °C for 0.5 h shows decreases of the surface resistivity from 38 Ω/square to 25 Ω/square. During the reactions of the two films with H_2S color change of the films from brown to green and from yellowish green to green was observed, respectively. The XPS analyses of the films from the reaction for 0.5 h at 60 °C were carried out before and after exposure to H_2S. The spectrum of

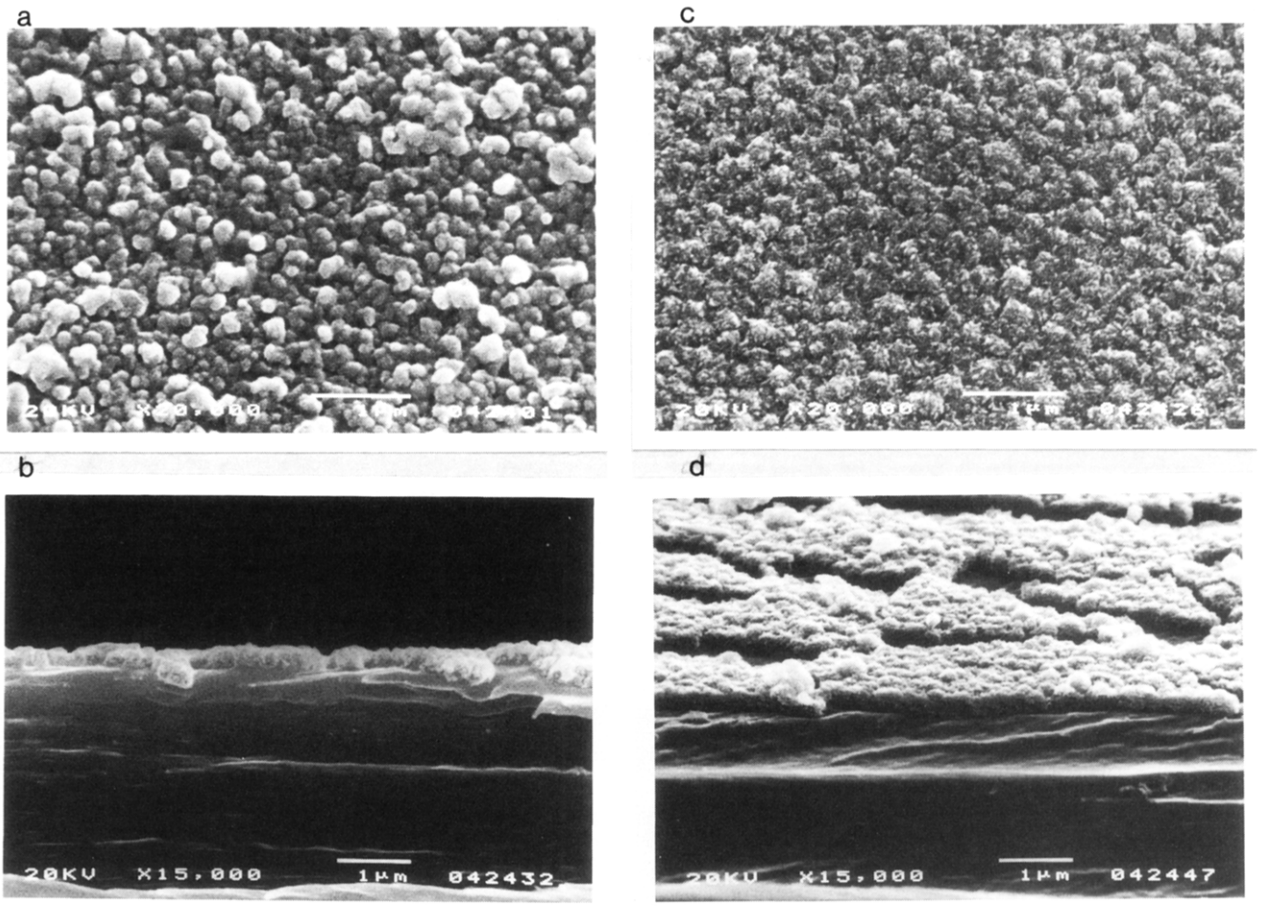


Figure 3. Scanning electron micrographs of the Cu_xS–PET film prepared by immersing the PET films pretreated with PEI into the aqueous solution of $CuSO_4$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) at 60 °C for 0.5 h ((a) surface and (b) cross-section) and of the Cu_xS–PET film prepared at 70 °C for 2 h ((c) surface and (d) cross section). The PET films were pretreated with a methanol solution of PEI for 48 h before deposition of Cu_xS.

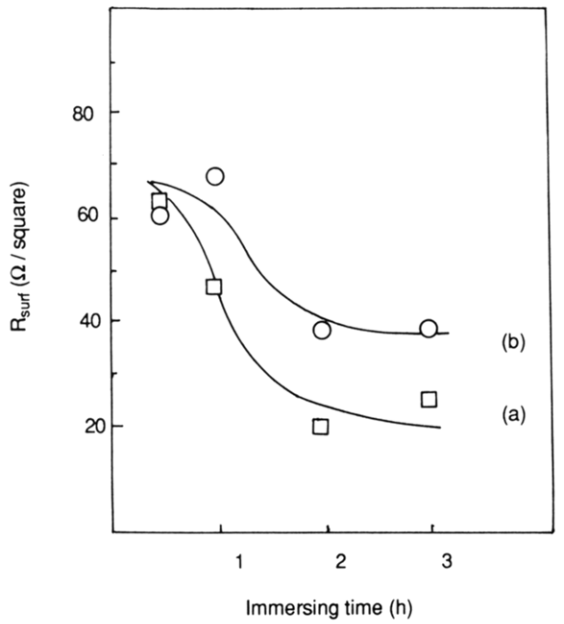


Figure 4. Change of the surface resistivity (R_{surf}) of poly(urethane) coated PET films during deposition of Cu_xS in the aqueous solution at (a) 70 °C and (b) at 60 °C.

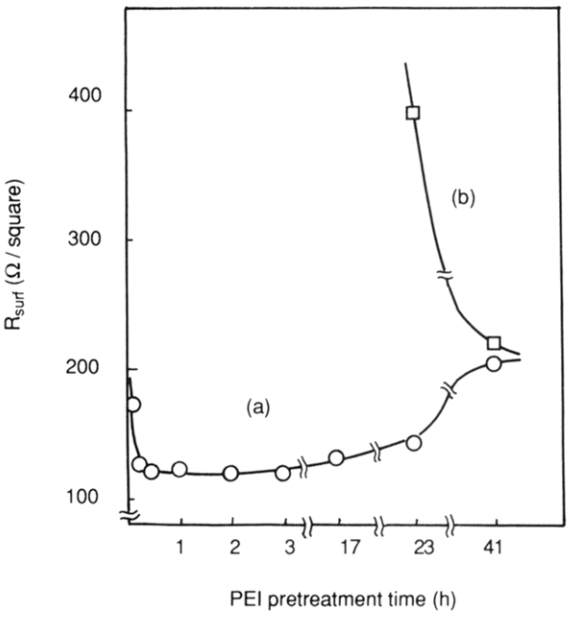
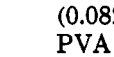


Figure 5. Dependence of the surface resistivity (R_{surf}) of the Cu_xS–PET films on the period of pretreatment with a methanol solution of PEI (1%). The PET films (a) with and (b) without the poly(urethane) coating were immersed in the aqueous solution of $CuSO_4$ (0.10 M) and $Na_2S_2O_3$ (0.10 M) at 60 °C for 0.5 h.

the film before exposure to H_2S shows similar peaks to Figure 2c, while the spectrum after the exposure is similar to Figure 2a which is identical with that of CuS.

Copper Sulfide Deposited Films of the Other Polymers. Deposition of copper sulfide on the PVA film having OH functions in the molecule is examined. Immersing the biaxially oriented PVA film in the Cu_xS sol prepared *in situ* for 2 h at 70 °C leads the formation of the coated film with 50 Ω/square. The film without PEI

Table II. Cu_xS–PET Films Prepared after Pretreatment with Silicon-Containing Compounds. Effect of the Silicon-Containing Compounds on the Surface Resistivity

silicon-containing compounds	PET-Cu_xS films surface resistivity (Ω/square) pretreatment in aqueous solution	pretreatment in methanol solution
$MeSi(OMe)_3$	100–150[b]	a
$(CH_2{=}CH)Si(OEt)_3$	a,b	a
$H_2N(CH_2)_3Si(OEt)_3$	60–80	60–70
$H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$	a	70–90
	a	a
$CH_2{=}C(Me)COO(CH_2)_3Si(OMe)_3$	90–100[b]	a
$HS(CH_2)_3Si(OMe)_3$	100[c]	100–150
$Me_3SiNHSiMe_3$	a,b	a

[a] No or poor amount of Cu_xS film is deposited on the PET film surface. [b] The pretreatment was carried out in aqueous solution containing acetic acid (pH = 4.0). [c] The pretreatment was carried out in aqueous solution containing acetic acid (pH = 5.0).

treatment does not undergo deposition of the copper sulfide under the same conditions.

Deposition of copper sulfide on the PVA film proceeds smoothly when the PVA film is pretreated in an aqueous solution containing potassium iodide (1.9 M) and iodine (0.082 M) at room temperature for 2 h.[7] Immersing the PVA film in the Cu_xS sol prepared in situ for 6 h at 70 °C gives the Cu_xS–PVA film, which shows the electrical conductivity of 32 S cm^{-1} along the direction of the surface. Its electrical conductivity follows an Arrhenius type equation with a negative activation energy of −0.40 kJ mol^{-1} in accordance with the electric conduction through Cu_xS.[4,7] The Cu_xS–PVA film, however, is not conductive along the direction of thickness.

ID-300 film is also converted to the electrically conducting film by immersing in the copper sulfide solution after PEI treatment to give the Cu_xS-ID-300 films with 30–100 Ω/square.

Discussion

The aqueous reactions of $CuSO_4$ with $Na_2S_2O_3$ at 50–70 °C cause deposition of the copper sulfides, Cu_xS, in various x values. Since reaction of $CuSO_4$ with $Na_2S_2O_3$ at room temperature gives a mixture of several copper thiosulfinite complexes such as $Na_2[Cu(S_2O_3)_2]$ and $[Cu(S_2O_3)(H_2O)_2]$, heating the solution seems to cause decomposition of the complexes to give CuS and/or Cu_2S depending on the conditions. In the reaction at 60 °C for 0.5 h the solution shows blue color indicating the presence of unreacted Cu(II) complexes in small amounts. The solution after the reaction at 70 °C for 2 h gives colorless solution, indicating complete conversion of the Cu(II) complexes to copper sulfides. The products in the reactions show quite different Cu to S ratio to each other probably due to variable ratio of CuS to Cu_2S. The former reaction gives the product with the composition of $Cu_{1.7}S$ based on the analytical results. Although it is not plausible to estimate the precise ratio of CuS to Cu_xS in the product based on the analytical results due to contamination of small amounts of thiosulfinite complexes which would disturb analytical results seriously, the product seems to contain Cu_2S as the main component based on the X-ray diffraction pattern of the powdery product. The latter reaction gives CuS based on the analytical result. The serious temperature influence on composition of the reaction products is attributed to the temperature-dependent equilibrium constants between the thiosulfinite complexes, difference of the decomposition rate of the complexes as well as solubility or deposition rate of CuS and Cu_2S in the aqueous solution.

As shown in Table I the Cu_xS–PET film prepared by immersing the PET film for 0.5 h at 60 °C in the aqueous solution of $CuSO_4$ and $Na_2S_2O_3$ shows brown color. The films obtained from the reaction for 2 h or the reaction at 70 °C show yellow to green yellow color. Engelken and McCloud reported properties of Cu_xS films prepared by electrodeposition on ITO substrate in various value of x to reveal that the Cu_xS films show brown color in x = 1.64–2.17 and green color in x = 1.06–1.39.[8] The dependence of the color of the Cu_xS–PET film on the x values in the present study agrees with that of the electrodeposited Cu_xS films. The $Cu_{1.7}S$–PET film prepared at 60 °C for 0.5 h shows higher surface resistivity than the CuS–PET film prepared at 70 °C for 2 h. Since CuS shows higher electrical conductivity than Cu_2S, the electrical conductivity of the CuS–PET film is reasonably higher than the $Cu_{1.7}S$–PET film having Cu_2S as a major component. X-ray diffraction patterns of the $Cu_{1.7}S$–PET and the CuS–PET film show only the peaks due to diffraction of PET probably due to low crystallinity of the copper sulfide deposited on the polymer film.

Morphology of the copper sulfide layer is considered to influence the surface resistivity in part. As observed in the scanning electron micrographs, the CuS–PET film by deposition at 70 °C for 2 h has the CuS particles with smaller size than the $Cu_{1.7}S$–PET from the reaction for 0.5 h at 60 °C. Higher electrical conductivity of the former film than the latter can be attributed to intrinsically higher electrical conduction of CuS than that of Cu_2S and to the smaller particle size of the Cu_xS in the former film than the latter. The thickness of the both Cu_xS layer on the polymer surface is 400 nm independent of the conditions of the Cu_xS deposition. As shown in Figure 1 the PEI pretreated PET film react with the Cu_xS solution at 70 °C to show decrease in the surface resistivity during the initial 2 h, while the Cu_xS–PET film prepared at 60 °C for 0.5 h shows surface resistivity of 105 Ω/square which does not decrease for further reaction at the temperature. As shown in Table I poly(urethane) precoated PET film undergo deposition of Cu_xS to show decrease in the surface resistivity during the initial 2 h both at 60 and at 70 °C. In all these cases the lowest surface resistivity is obtained in the reaction for 2 h. Since the thickness of the Cu_xS layer reaches maximum value (ca. 400 nm) in the reaction for 0.5 h, decrease in the surface resistivity in further reaction is attributed to change of morphology of the Cu_xS layer on the PET film surface. PEI pretreated PET film after deposition of Cu_xS on the surface at 60 °C seems to undergo the morphology change to little extent during the further reaction, while the film prepared at 70 °C and those from poly(urethane)-coated film show decrease in the surface resistivity during the reaction after initial 0.5 h deposition of Cu_xS.

(6) X-ray diffraction data of copper sulfides and oxides were taken from ASTM data. (a) CuS: *Powder Diffraction File Sets 6-10 (Revised). Inorganic Volume*; Smith, J. V., Ed.; American Society for Testing and Materials: Philadelphia, 1967; 6-0464. (b) Cu_xS ($1.86 < x < 1.96$): *Powder Diffraction File Set 23. Inorganic volume*; Smith, J. V., Ed.; American Society for Testing and Materials: Philadelphia, 1983; 23–958.

(7) Yamamoto, T.; Kubota, E. *Chem. Ind. (London)* **1986**, 531.

(8) Engelken, R. D.; McCloud, H. E. *J. Electrochem. Soc.* **1985**, *132*, 567.

Achievement of good quality of the Cu_xS film on the organic polymer film surface requires pretreatment with PEI or silicon-containing compounds shown in Table II. These compounds seem to play important roles as the binder between the inorganic metal sulfides and organic polymer film surface in formation of good contact between these materials. The functions of PEI and the organic silicon compounds are supposed as follows. The PEI, whose molecule can be adsorbed firmly on the surface of the polymer film, have NH groups which undergo partial protonation under the slightly acidic conditions for preparation of the Cu_xS–PET film. Since colloidal particles of copper sulfide have negative charge, they are adsorbed on the polymer film surface through attractive interaction between the Cu_xS particles and protonated PEI layer on the film surface. Organic silicon compounds in Table II having alkoxysilyl group undergo hydrolysis under the reaction conditions to give compounds with Si–OH group which can be bonded to the Cu_xS particles in the solution. On the other hand, amino, HS and methacryl groups contained in the silicon-containing compounds seem to be adsorbed on the organic polymer film. Thus, organic silicon compounds seem to help bind the inorganic and organic materials to give the polymer films coated with electrically conducting Cu_xS layer.

Although the procedure of preparation of the Cu_xS–polymer films in this study is applicable to other polymers with OH or C–O–C functions in the molecules such as PVA and ID-300, the pretreatment of the surface by PEI or silicon-containing compounds is required to obtain a good Cu_xS deposited film with high electrical conductivity. The OH function in the PVA does not help to adsorb the Cu_xS particles directly under the conditions.

Conclusion

Films of organic polymers such as PET, PVA, and ID-300 undergo deposition of the copper sulfide on the film surface to give the electrically conducting films. Pretreatment of the film by PEI or silicon-containing compounds is indispensable, while the poly(urethane) precoated PET film does not require the pretreatment before deposition of the Cu_xS. The Cu_xS–polymer films obtained in the present study will be utilized as optical devices or electrodes of optoelectrical reactions.