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ELECTROCHROMISM OF THE COMPOSITE FILM OF ETHYLENE-VINYL ALCOHOL COPOLYMER AND POLYPYRROLE

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ABSTRACT

The composite film of ethylene-vinyl alcohol copolymer (EVOH) and polypyrrole (PPy) were prepared by the electrochemical polymerization of pyrrole on an EVOH film containing lithium perchlorate coated on Indium-tin oxide (ITO). When a potential was varied from -1.0 V to 1.0 V, the color of the composite film changed reversibly from yellow to brown. The difference in absorbance (ΔA, 0.1-0.15) at 800 nm between the application of 1.0 V and -1.0 V in UV/VIS spectra of the composite film did not exhibit a pronounced decrease until ca.7000 cycles. In contrast to this behavior, the ΔA of a single PPy film rapidly dropped with an increasing cycle number and approached 0 within ca. 1000 cycles. This result indicates that the durability against the repeated application of potentials markedly improved in the composite film.

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INTRODUCTION

Conducting polymers are attractive materials for optical control and display devices because of the electrochromism, that is, the ability of a material or system to change color reversibly in response to an applied potential. This color change is attributed to the difference of the electronic structure between the oxidized (conducting) and reduced (insulating) states of the polymer. Among a variety of materials that exhibit electrochromism [1-7], polypyrrole (PPy) is one of the promising materials for electrochromic display because PPy can be reversibly switched between the oxidized and reduced states [8, 9]. However, a short cycle life time, probably due to chemical or electrochemical corrosion of the film, is a major disadvantage of the electrochromic devices using PPy and the other conducting polymers in the practical application. Recently, it was reported that the mechanical properties of the film are considerably improved by use of the composites of PPy and other polymers [10, 11]. The present paper describes improvement of the cycle life time by use of the composite film of ethylene-vinyl alcohol copolymer (EVOH) and PPy.

EXPERIMENTAL

Materials

The ethylene-vinyl alcohol copolymer (EVOH, EP-F101) with the feed ethylene content of 32 mol% and Melt Index (MI, 190°C, load 2160 g) of 1.3 g/10 min. was obtained from Kuraray Co. Ltd. Special reagents grade pyrrole monomer, propylene carbonate, ethanol, acetonitrile, dimethylsulfoxide (DMSO), and lithium perchlorate were used without further purification.

Preparation of Films

A prescribed amount of lithium perchlorate was added to a 50 g/l solution of EVOH in DMSO. The solution was cast on an Indium-Tin oxide (ITO) which was washed beforehand with 2-propanol and dried, and subsequently dried at 130°C *in vacuo*. The electrochemical polymerization was carried out at a constant current density (0.15 mA$\cdot$ cm^{-2}) using a solution containing ethanol, 0.1 M pyrrole and 0.1 M lithium perchlorate in a cell comprising two electrodes. The ITO on which EVOH containing lithium perchlorate was coated, and platinum were used, respectively, as anode and cathode. A PPy single film was prepared in the same manner as the preparation of the composite films. The films at the polymerization time of 10 minutes were used for the measurements of UV-VIS spectra and cyclic voltammogram.

Measurements

Surface electric resistance was measured at ambient temperature by the conventional four-probe method using a digital multimeter (Model TR8652, Advantest Co.). The electric conductivity measurement was carried out at ambient temperature with an impedance analyzer (Model 4194A, Yokokawa Hewlett-Packard Co.). The measurement of UV/VIS spectra of the EVOH-PPy composite film coated on the ITO glass in ethanol containing lithium perchlorate under the repeated application of potentials (±1.0 V, 10 s) was made on an UV-2200 spectrometer (Shimazu Co. Ltd.). The cyclic voltammetry measurement of the composite film was carried out using a functional generator Model 4500A (Kikusui Electron Co.) and potentiostat/galvanostat HA-301 (Hokuto Denko Ltd.). A solution (0.2 M) of lithium perchlorate in acetonitrile, propylene carbonate, ion-exchanged water, or ethanol was used as an electrolyte solution. The scanning electron microscopy (SEM) measurement was performed on a JSM-840 machine (Japan Electron Co. Ltd.).

RESULTS AND DISCUSSION

Preparation Condition of the Composite Films

The effect of lithium perchlorate concentration in EVOH on the electrochemical polymerization of pyrrole was investigated. When the lithium perchlorate concentration was 0.125 g/g EVOH,the polymerization of pyrrole proceeded smoothly in an ethanol solution of 0.1 M pyrrole and 0.1 M lithium perchlorate at 20°C. However, the polymerization did not take place at the salt concentration of 0.1 g/g EVOH or less, and lithium perchlorate precipitated in the EVOH film at the concentration of 0.15 g/g EVOH or above. When acetonitrile, propylene carbonate or water was used as a solvent of the electrolytic solution, the electrochemical polymerization did not occur. Successful polymerization in ethanol may be attributed to the solubility parameter of ethanol (8.5) close to that of EVOH (8.3) (propylene carbonate 11.0, acetonitrile 11.9, water 12.8). Regarding the polymerization temperature, although the electrochemical polymerization proceeded at 20°C or above, the reaction did not occur at 10°C or less. Because low temperature polymerization of PPy is preferred in general, reaction temperature was fixed to 20°C.

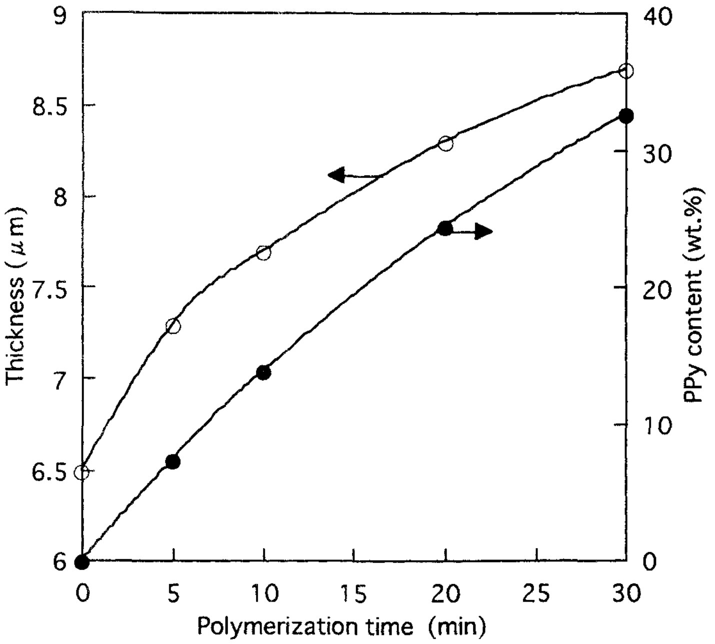

Figure 1. Relationship between polymerization time and thickness of the composite film, or PPy content in the composite film: (O) Thickness, (●) PPy content.

Conductivity and SEM Morphologies of the Composite Films

The electrochemical polymerization of pyrrole on the EVOH film containing lithium perchlorate of 0.125 g/g EVOH was carried out at 20°C in an ethanol solution of 0.1 M pyrrole and 0.1 M lithium perchlorate. Figure 1 shows the relationship between the polymerization time and thickness of the composite film measured by a micrometer, or the PPy content in the composite film calculated from the change of the weight. As is obvious from the figure, the thickness and the PPy content of the composite film increased with an increase of the polymerization time, indicating that the polymerization of pyrrole proceeded smoothly until 30 minutes. The relationship between the polymerization time and the surface resistance of the composite film at the ITO electrode and solution sides is shown in Figure 2. The surface resistance at the electrode side is lower than that at the solution side, indicating that the PPy layer is formed preferably at the electrode side. Electric conductivity rapidly increased until ca. 5 minutes and thereafter slowly increased as also shown in Figure 2.

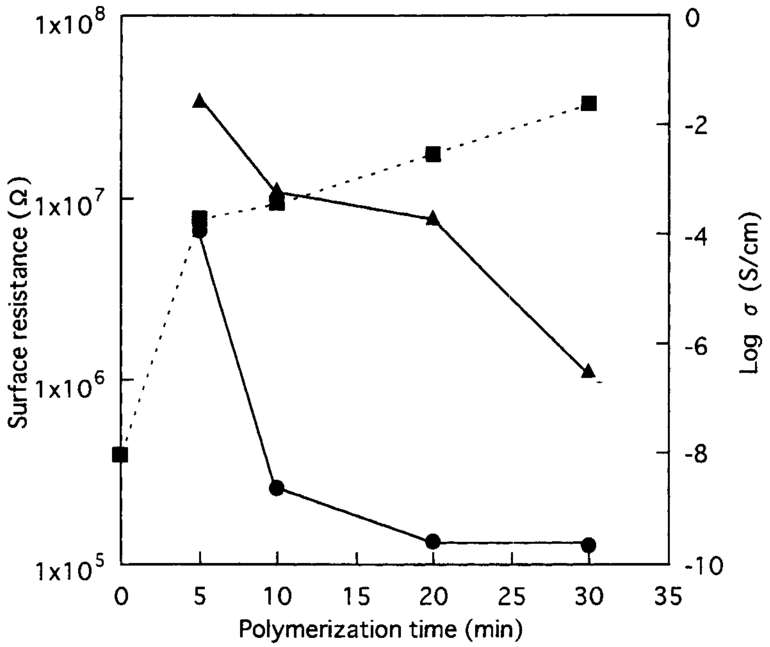

Figure 2. Relationship between polymerization time and surface resistance at the ITO electrode side and the solution side, or electric conductivity of the composite film: (●) Surface resistance at the electrode side, (▲) Surface resistance at the solution side, (■) Electric conductivity.

The SEM micrographs of the composite films at the electrode side and the solution side are shown in Figure 3. A precise PPy layer is already formed on the electrode side at 5 minutes. On the other hand, a PPy layer at the solution side is composed of the larger particles as compared with those of the electrode side, and has many hollows at 5 minutes, in agreement with the lower surface resistance at the solution side. The number of the hollows gradually decreased and the PPy particles were densely coagulated at 20 minutes.

Electrochromism of the Composite Films

Figure 4 shows the UV/VIS spectral change of the EVOH-PPy composite film in an ethanol solution of 0.2 M lithium perchlorate between the application of 1.0 V and -1.0 V with increasing cycle number of the redox process. The absorptions at 800-900 nm and 300-400 nm pertain to the oxidized and reduced PPy,

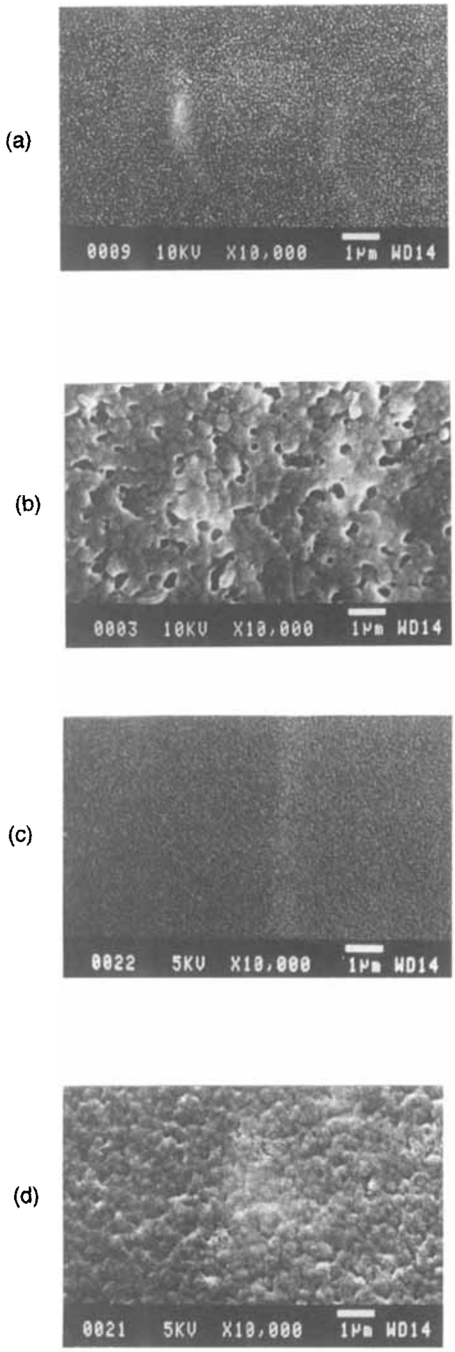

Figure 3. The SEM micrographs of the composite films at the electrode side and the solution side at various polymerization times: (a) Electrode side, 5 minutes; (b) Solution side, 5 minutes; (c) Electrode side, 20 minutes; (d) Solution side, 20 minutes.

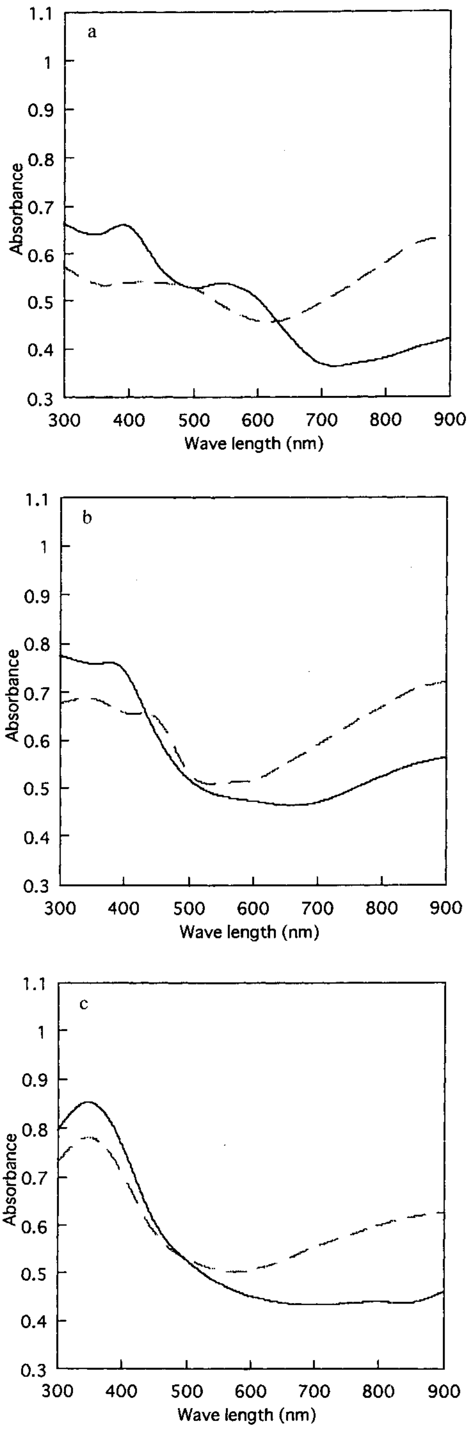

Figure 4. The UV/VIS spectral change of the composite film between the application of 1.0 V and -1.0 V with an increasing cycle number of the redox process:(a) 50 cycles, (b) 400 cycles, (c) 5000 cycles, (d) 10000 cycles, (–) -1.0 V undoping, (--) 1.0 V, doping.

(continued)

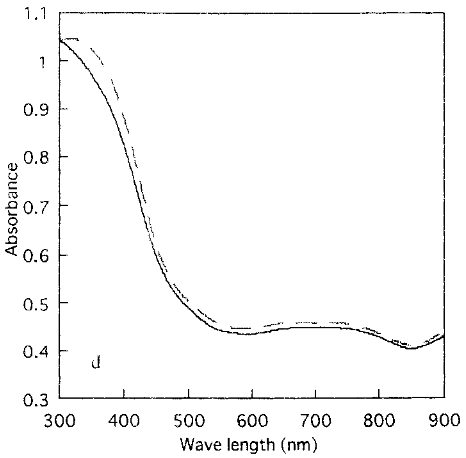

Figure 4. Continued

respectively. When the potential was varied from -1.0 V to 1.0 V, the absorbance at 300-400 nm decreased, whereas the one at 800-900 nm increased, accompanied by the color change from yellow to brown. However, the change of the absorption pattern gradually became smaller with an increasing cycle number, and did not appear at ca.10000 cycles (Figure 4d).

The difference of absorbance (ΔA) at 800 nm between the application of 1.0 V and -1.0 V versus cycle number of the redox process is shown in Figure 5. In a single PPy film, the DA rapidly dropped with an increasing cycle number and approached 0 within 1000 cycles. In contrast to this behavior, the ΔA (0.1-0.15) did not exhibit a pronounced decrease until ca. 7000 cycles in the composite film.

The redox process of the EVOH-PPy composite film and the PPy film was also monitored by the cyclic voltammetry scanned at 160 mV/s from 1.0 V to -1.0 V in an ethanol solution of 0.2 M lithium perchlorate. The relationship between the quantity of electricity per one cycle and cycle number of the redox process for the composite film and the PPy film is shown in Figure 6. As is obvious from the figure, the quantity of electricity per one cycle rapidly decreased and approached 0 within 1000 cycles in the PPy film. In the composite film, the quantity of electricity slowly decreased and the half value of the maximum quantity was still kept at ca. 3000 cycles. These results indicate that the durability against the repeated redox reactions markedly improved in the composite film.

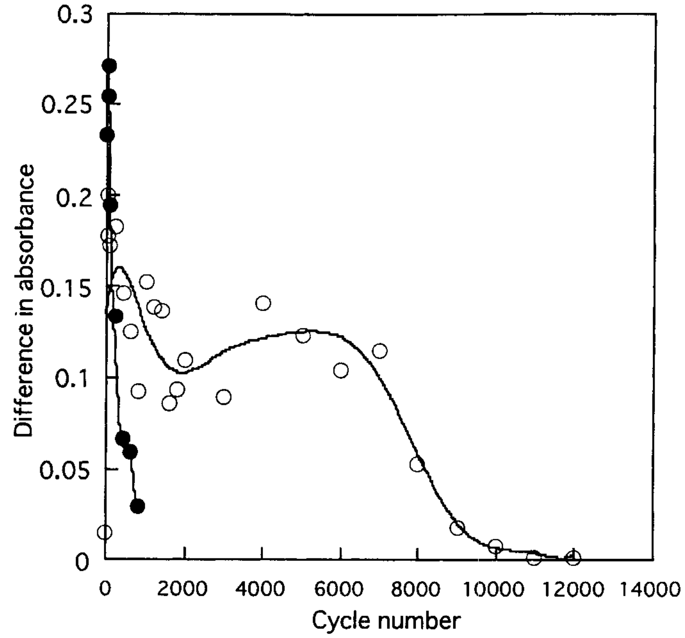

Figure 5. The difference in absorbance at 800 nm between the application of 1.0 V and -1.0 V (ΔA) versus cycle number of the redox process for the EVOH-PPy and the PPy films: (○) EVOH-PPy film, (●) PPy film.

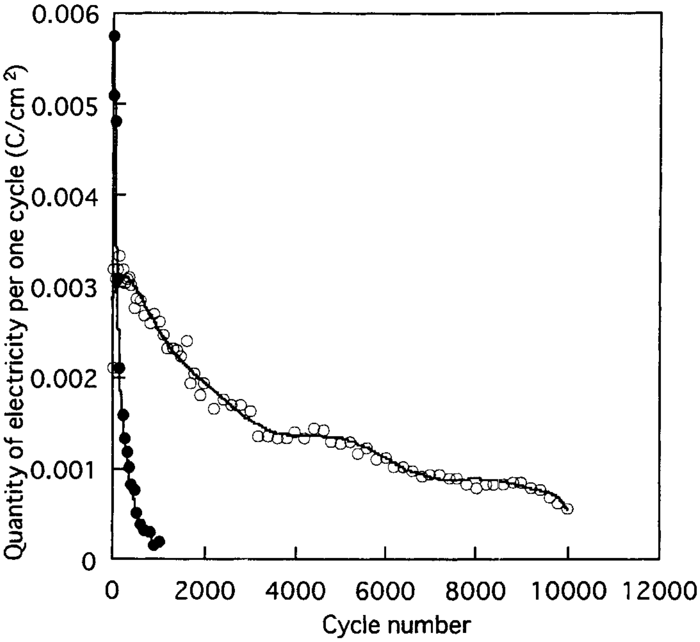

Figure 6. Relationship between the quantity of electricity per one cycle and cycle number of the redox process in the cyclic voltammogram scanned at 160 mV/s from 1.0 V to -1.0 V for the EVOH-PPy and the PPy films: (○) EVOH-PPy film, (●) PPy film.

CONCLUSION

By optimizing the electrochemical polymerization condition of pyrrole on the EVOH film, the EVOH-PPy composite film coated on ITO was successfully prepared. The color of the obtained composite film changed reversibly from yellow to brown when a potential was varied between -1.0 V and 1.0 V. Life cycle time of the composite film evaluated by the UV/VIS spectral change and the quantity of electricity per one cycle in the cyclic voltammogram markedly increased as compared with that of the PPy single film. The EVOH-PPy composite film is thought to be a promising material for the practical application in the electrochromic display devices.

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