Conducting Polypyrrole Composite Thin Films Chemically Prepared by Spreading on Surface of Aqueous Solution Containing Oxidizing Agent

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Synopsis

Polypyrrole–PMMA composite films have been prepared with the chemical oxidative polymerization by spreading the water-insoluble solvent solution of pyrrole and PMMA mixture on the surface of the aqueous solution containing $K_2S_2O_8$, the oxidizing agent. The conductivity of the films increases rapidly, passes through a plateau, and then decreases gradually as the reaction time increases. The conductivity of the oxidized side of the film is higher by over 1 order of magnitude than that of the evaporated side. It is due to the fact that the former is rich in polypyrrole while the latter is rich in PMMA. The thickness of the films can be controlled by adjusting the PMMA concentration. However, the lower limit of the film thickness is practically in submicron order. The relationship between the transmittance and the logarithm of the conductivity of the films gives a straight line with a gradient, ca. -8. The conductivity of the films is stable on silicagels in a desiccator over 2000 h at 25°C. The conductivity of the film is, however, very sensitive to the moisture in atmosphere and gives rise to decrease with humidity.

INTRODUCTION

Polypyrrole has attracted great interest for its good conductivity and high stability.[1] Polypyrrole films are studied extensively for a variety of applications, including electrode materials,[2,3] electric devices,[4-6] and some kinds of sensors.[7] The polypyrrole films—either homogeneous or composite—are prepared by electrochemical oxidative polymerization. But the procedure of electrochemical polymerization is more or less complicated and the area of the prepared films depends on that of electrodes, so that it is difficult to prepare large area films by that method. On the other hand, polypyrrole is also prepared by the chemical oxidative polymerization. However, the polypyrrole prepared by chemical polymerizations is usually formed as bulky powders —so-called "pyrrole blacks" and is poor in conductivity.[8] In order to prepare conducting polypyrrole films with chemical method, some hybridization methods of polypyrrole with supporting materials are proposed.[9-11]

This article describes the new preparation method of polypyrrole composite films with the chemical oxidative polymerization by spreading on surface of aqueous solution containing oxidizing agent. The effects of the preparation conditions on the conductivity and the transmittance of the composite films, the lower limit of the film thickness, and the stability of the conductivity are investigated.

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EXPERIMENTAL

Polypyrrole composite films were usually prepared as follows: two glass plates making a slit with a given interval were put on the polypropylene vat filled with aqueous solution containing a given concentration of oxidizing agent. After dissolving a given amount of matrix polymer, pyrrole, and spreading assistant in water-insoluble solvent, a given quantity of the solution was poured onto the surface of the oxidizing solution within the slit. Then it was spread by sliding one plate to a given distance. Pyrrole was polymerized at the interface between the pyrrole–matrix polymer and oxidizing agent solution accompanying formation of the composite film as the solvent evaporated. The area of the film was controlled by adjusting the spreading area. After a given reaction time, the composite film was taken out and immersed in pure water for removal of excess oxidizing agent, and dried under vacuum at room temperature. In this work, poly(methyl methacrylate) (PMMA; M_n = 390000) was used as a matrix polymer, benzoic acid as a spreading assistant, 2-butanone as a water-insoluble solvent, and potassium peroxodisulfate ($K_2S_2O_8$) as an oxidizing agent. The same amount of benzoic acid with PMMA was used to get the optimum conditions for spreading of pyrrole–PMMA solution on the aqueous solution at a proper interfacial tension. Each film was prepared by pouring 0.5 mL of pyrrole–PMMA solution into the slit with 0.5 cm interval and spreading it to 13×10 cm^2 under the same atmospheric condition: 25°C, 40% RH.

The conductivity of the films was measured using the standard four-probe technique under 10^{-3} torr at 40°C for elimination of absorbants and moisture from the film surface. The transmittance was measured with a Shimadzu UV-240 spectrophotometer at the wavelength 600 nm. The thickness of the films was measured with a Kosaka Laboratory Ltd. SP-11 surface roughness tester. The surface structures of the films were investigated by observation of scanning electron micrographs with a JEOL JSM-T300 scanning microscope and of ATR spectra with a Nicolet 5DX FT-IR spectrophotometer. Chemicals used in this work were all of special reagent grade and used without further purification, except for pyrrole and PMMA. Special reagent grade pyrrole was further purified by distillation before use. PMMA was prepared by a usual pearl polymerization and purified by reprecipitation from acetone.

RESULTS AND DISCUSSION

The pyrrole–PMMA composite films prepared by this method are black and semitransparent and looked like uniform—a so-called "polymer-alloy."

The effects of the preparation conditions on the conductivity and the transmittance of the composite films are shown in Figures 1 and 2. The evaluated films have been prepared on the oxidizing solution containing various concentrations of $K_2S_2O_8$ with the solution; PMMA/pyrrole/benzoic acid/2-butanone = 1/1/1/10. Figures 1 and 2 show the effect of the reaction time on the conductivity and the transmittance at 600 nm, respectively. The conductivity of the PMMA homogeneous film prepared with the solution containing no pyrrole is less than 10^{-9} S/cm. At higher concentration of the oxidizing agent, the conductivity of the films increases rapidly within 15 min, passes through a plateau, decreases gradually, and turns out to be an insulator
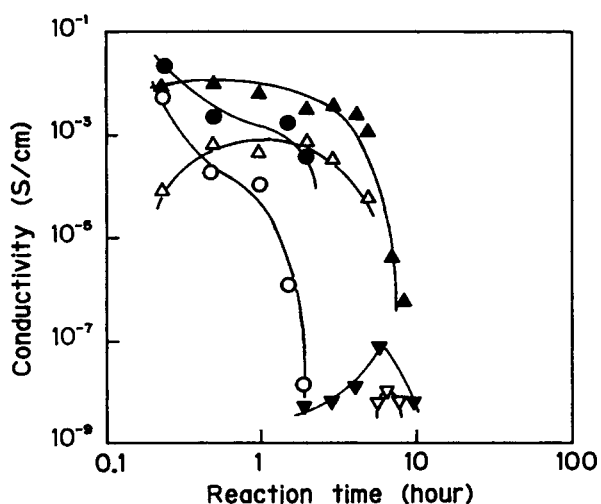
Fig. 1. Effect of the reaction time on the conductivity of the composite films at various concentrations of $K_2S_2O_8$: (O) 0.1M, evaporated side; (●) 0.1M, oxidized side; (△) 0.05M, evaporated side; (▲) 0.05M, oxidized side; (▽) 0.01M, evaporated side; (▼) 0.01M, oxidized side.

as the reaction time increases; but at lower concentration it does not increase very much. The conductivity of the side that has been contacted with the oxidizing solution (oxidized side) is higher by over 1 order of magnitude than that of the other side from which the solvent evaporated (evaporated side). The transmittance of the films is higher with the lower conductivity.

In Figure 1, the conductivity of the film prepared on the solution containing 0.05M of $K_2S_2O_8$ is the highest and most stable, so that the following investigations are carried out using the films prepared at this concentration of $K_2S_2O_8$ fixing the reaction time to 1 h.
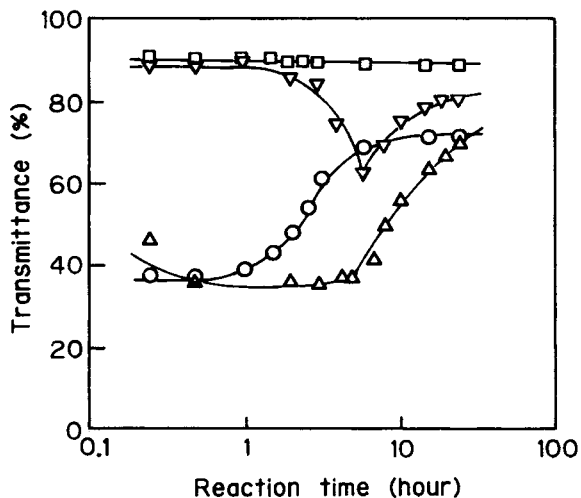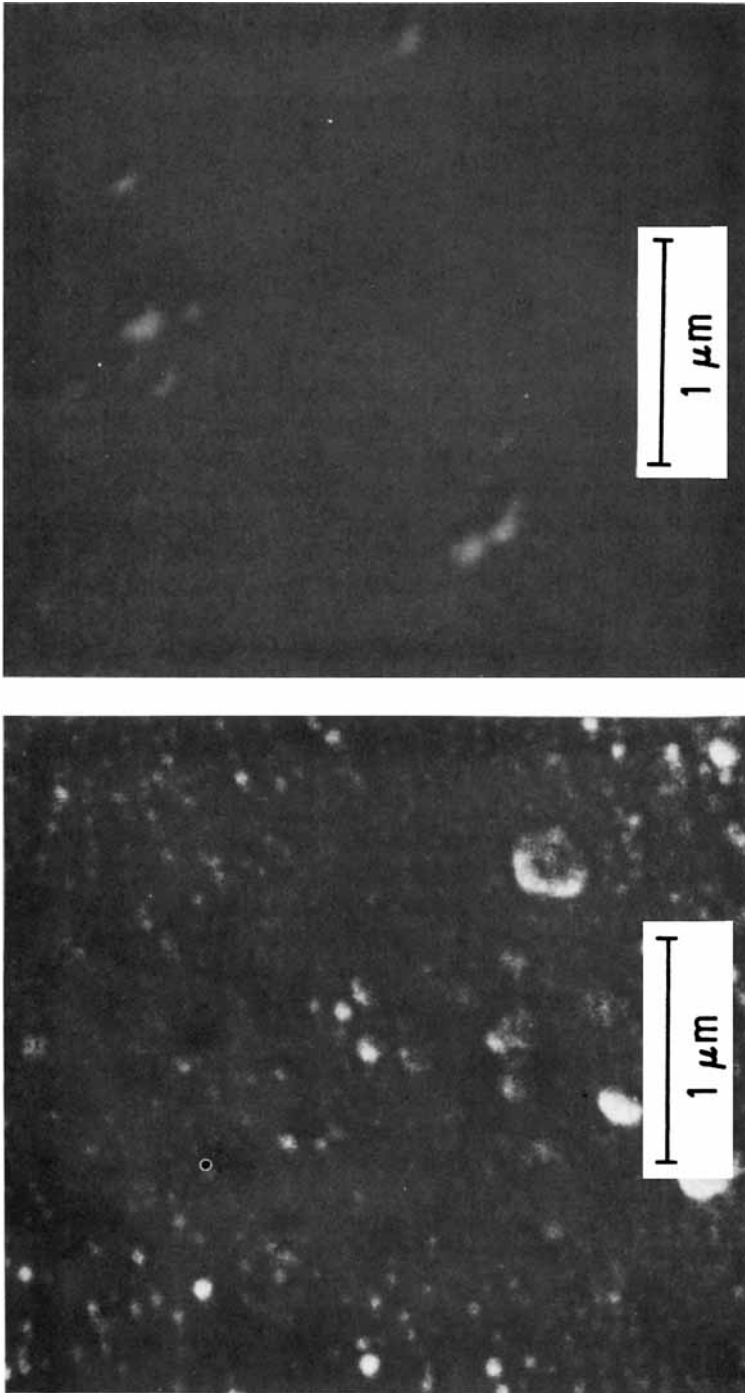

Fig. 2. Effect of the reaction time on the transmittance of the composite films at various concentrations of $K_2S_2O_8$: (O) 0.1M; (△) 0.05M; (▽) 0.01M; (□) 0.1M, PMMA homogeneous film.

(A) oxidized side　　　　　(B) evaporated side

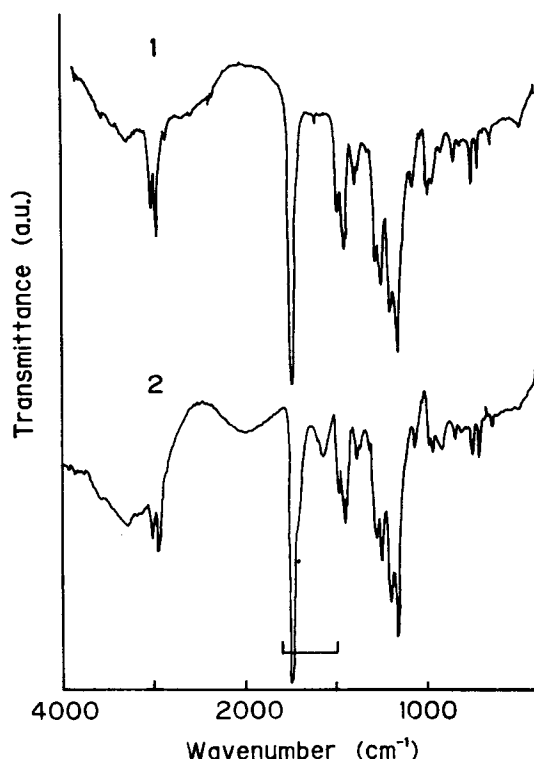Fig. 3.　Scanning electron micrographs of both surfaces of the composite film.

Fig. 4. FT-IR spectra (transparent) of the films prepared by this method: (1) PMMA homogeneous film; (2) composite film.

Typical scanning electron micrographs of the composite films are shown in Figure 3. As shown, a lot of polypyrrole particles appear on the oxidized side, while the surface of the film is smooth on the evaporated side.

Figure 4 shows a typical FT-IR transparent spectrum of the composite film (2) and the PMMA homogeneous film (1) prepared with the solution; PMMA/benzoic acid/2-butanone = 1/1/10. The IR spectrum of the composite film looks like the PMMA spectrum overlapped with the bands at 1500–1620 cm^{-1} assigned to the stretching vibrations of pyrrole rings.

Figure 5 shows the ATR spectrum of the bands of the pyrrole rings at various reaction times, standardized by the band at 1720 cm^{-1} assigned to the stretching vibrations of the carbonyl groups of PMMA with regard to both sides of the films used in Figures 1 and 2. As the reaction time increases, the intensity of the pyrrole bands decreases after it appeared within 1 h, while the new bands appear at about 1650 cm^{-1}, which probably assigned to the oxidative decomposition products of the pyrrole rings, and its intensity increases in the spectrum of the oxidized side. The conductivity of the oxidized side decreases in a similar trend with decreasing of the pyrrole bands (see Fig. 1). On the other hand, the pyrrole bands do not appear in the evaporated side, so that the surface layer of that side is almost all covered with PMMA. In the evaporated side, the current passes through the thin insulating layer of PMMA, so that the conductivity of the evaporated side is lower than that of the oxidized side.
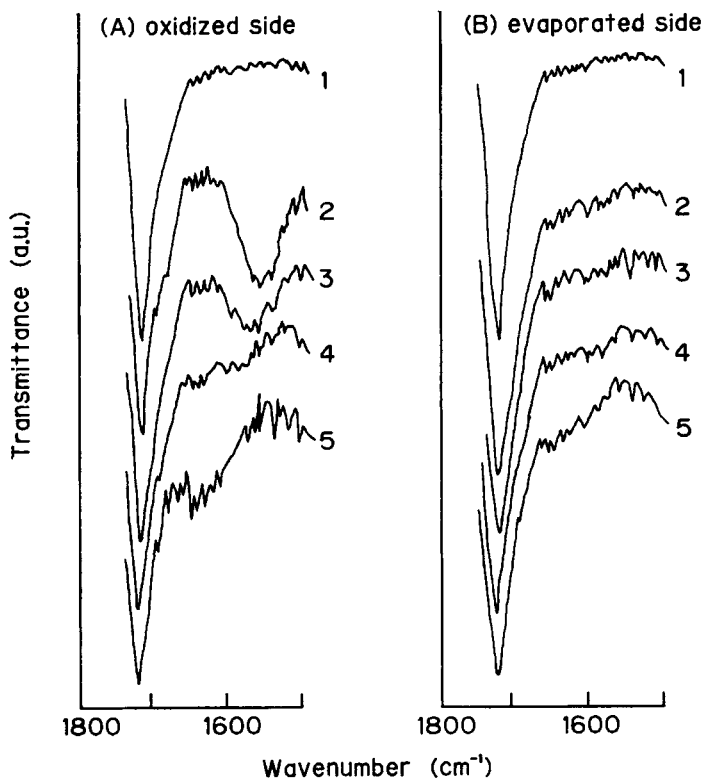
Fig. 5.   FT-IR spectra (ATR) of the composite films at various reaction time (h): (2) 1; (3) 5; (4) 8; (5) 24; (1) 1, PMMA homogeneous film.
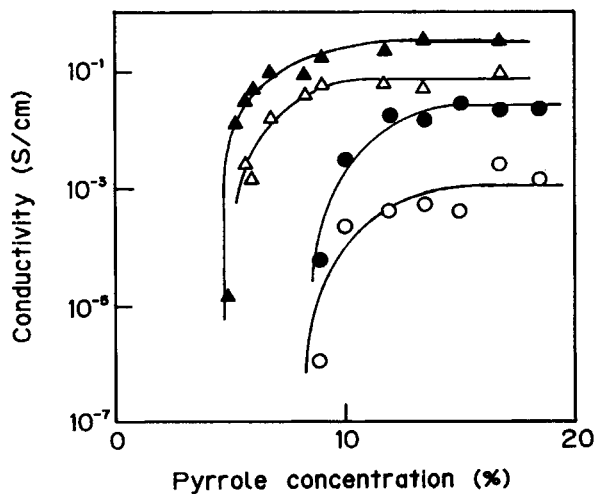

Fig. 6.   Effect of pyrrole concentration on the conductivity of the composite films at various concentrations of PMMA: (o) 10%, evaporated side; (●) 10%, oxidized side; (△) 1%, evaporated side; (▲) 1%, oxized side.
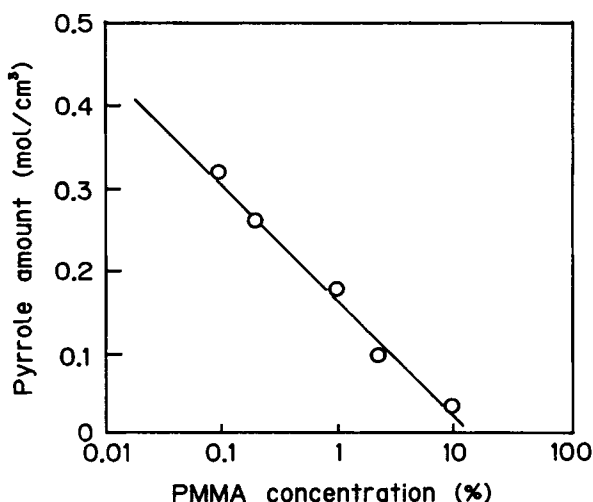
Fig. 7. The minimum pyrrole amount per unit volume of the composite film required to saturate the conductivity as a function of PMMA concentration.

The lower limit of the thickness of the composite films is shown in Figures 6–9. Figure 6 shows the effect of pyrrole concentration on the conductivity of the films prepared with the solutions containing various concentrations of PMMA. The conductivity of either evaporated side or oxidized side increases and reaches to saturation as pyrrole concentration increases.

Figure 7 shows the minimum pyrrole amount per unit volume of the composite films required to saturate the film conductivity as a function of PMMA concentration. That amount increases as PMMA concentration decreases. It is due to the localized distribution of polypyrrole perpendicularly to the film surface.
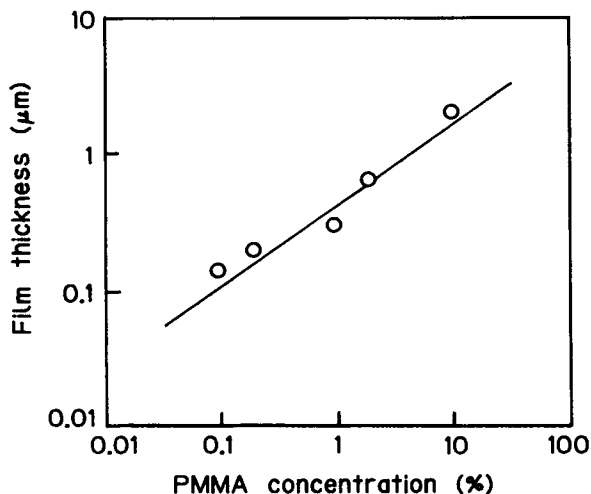

Fig. 8. The thickness of the composite films with saturated conductivity as a function of PMMA concentration.
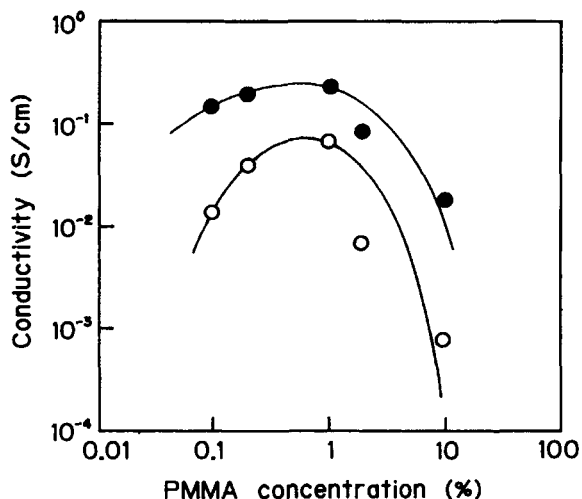
Fig. 9. The saturated conductivity of the composite films as a function of PMMA concentration: (○) evaporated side; (●) oxidized side.

The variations in some characteristics of the composite films prepared with the solution containing the minimum pyrrole amount required to saturate the film conductivity as a function of PMMA concentration are shown in Figures 8–10. As shown in Figure 8, the film thickness can be controlled by adjusting PMMA concentration. However, from Figure 9, the saturated conductivity of the films decreases at the concentration below about 1% of PMMA, although it increases above this concentration, as PMMA concentration decreases. Consequently, the practical lower limit of the film thickness is in submicron order corresponding to about 1% of PMMA. As shown in Figure 10, the transmittance of the films is higher with the lower conductivity, similarly to the aspects shown in Figures 1 and 2.
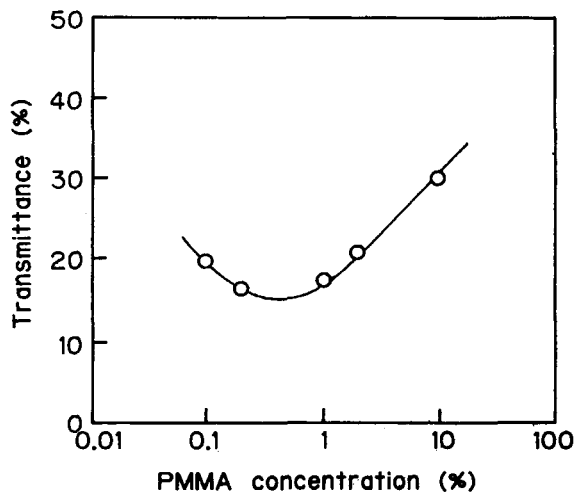

Fig. 10. The transmittance of the composite films with saturated conductivity as a function of PMMA concentration.
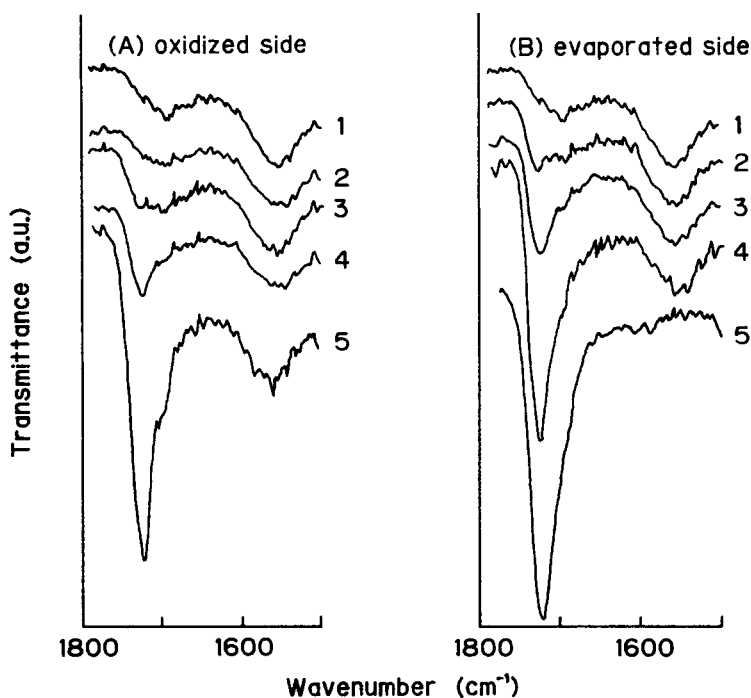
Fig. 11. FT-IR spectra (ATR) of the composite films when the conductivity saturated at various concentrations of PMMA: (1) 0.1%; (2) 0.2%; (3) 1.0%; (4) 2.0%; (5) 10.0%.
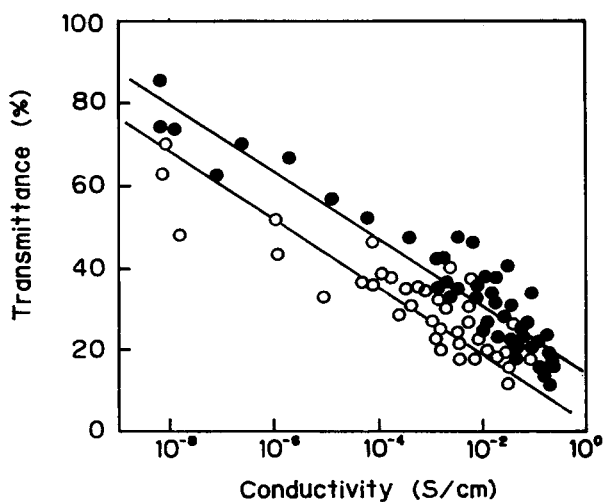

Fig. 12. The relationship between the transmittance and the logarithm of the conductivity of the composite films: (○) evaporated side; (●) oxidized side.
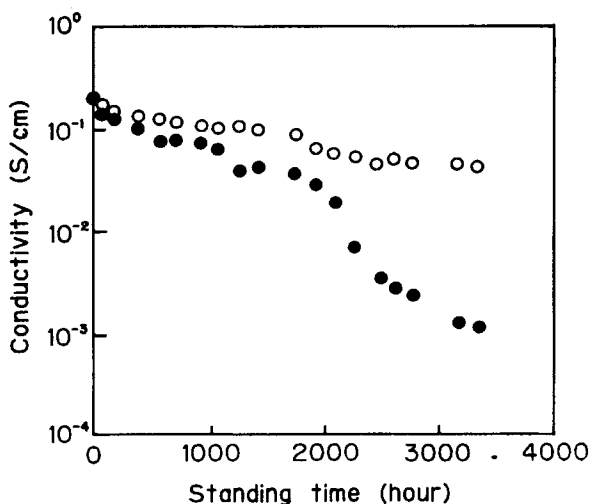
Fig. 13. The stability of the conductivity of the composite film: ($\bigcirc$) 25°C, in dry state; ($\bullet$) 25°C, in 40% RH atmosphere.

Figure 11 shows the peak strength of the carbonyl groups of PMMA at various concentrations of PMMA, standardized by the bands assigned to the pyrrole rings with regard to both sides of the films used in Figures 7–10, except for the case of 10% of PMMA in the evaporated side, in which the spectrum of pyrrole rings does not appear at all. In both sides, the peak strength of carbonyl groups decreases as PMMA concentration decreases. At sufficiently low concentration of PMMA, the surface of the film is almost all covered with polypyrrole. Nevertheless, the conductivity of the film decreases at the concentration below about 1% of PMMA (see Fig. 9). It is considered that the defects in conducting paths of polypyrrole are formed in the composite film at too low a concentration of the matrix polymer.

Figure 12 shows the relationship between the transmittance and the logarithm of the conductivity of all the composite films prepared in this work. Their correlation is given a straight line. On both oxidized and evaporated sides, the line has the same gradient, ca. −8. It is very difficult to prepare the composite films with high transmittance and conductivity by this method.

The stability of the conductivity of the oxidized side of the composite films is shown in Figure 13. The conductivity is stable on silicagels in a desiccator over 2000 h. However, even at the same temperature (25°C), the conductivity of the film standing in the 40% RH atmosphere decreases much faster than that of the film in the desiccator.

Khulbe and Mann have proposed the two oxidizing mechanisms of peroxodisulfate in aqueous solution.[12] It is stated that this is the reagent counterpart to the electrochemical polymerization.[1] One is the normal redox system (redox potential = 2.01 V; $S_2O_8^{2-}$, 0.8 V; pyrrole) according to the following scheme:

$$S_2O_8^{2-} + 2e^{-1} = 2SO_4^{2-} \tag{1}$$

And the other is the system in which peroxodisulfate behaves as a dissociative initiator for polymerization according to the following scheme:

$$S_2O_8^{2-} \rightarrow 2SO_4^- .$$ (2)

$$SO_4^- . + H_2O \rightarrow HSO_4^- + \cdot OH$$ (3)

$$2 \cdot OH \rightarrow H_2O + 1/2O_2$$ (4)
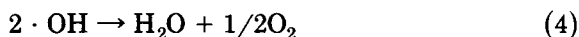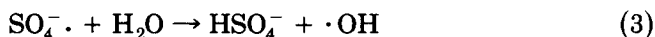
Here we propose that these sulfate radical ions initiate the polymerization of pyrrole by normal radical mechanism and spontaneously form charge transfer complex with formed polypyrrole (doping). Those radical ions turn to sulfate ions according to eq. (3). But the lost radical ions are compensated with excess peroxodisulfate in the oxidizing solution. Oxygen generated according to eq. (4) seems to decompose pyrrole rings at prolonged contact with the oxidizing solution (see Fig. 5). After being parted from the oxidizing solution and dried, however, it is considered that only decomposition of the polypyrrole–sulfate anion radical complex occurs with the water in the atmosphere, according to eq. (3). Thus, the conductivity of the films is very sensitive to the moisture in atmosphere and gives rise to decrease with humidity.

CONCLUSION

Polypyrrole–PMMA composite films are prepared with the chemical oxidative polymerization by spreading the water-insoluble solvent solution of pyrrole and PMMA mixture on the surface of the aqueous solution containing $K_2S_2O_8$. The conductivity of the films depends upon $K_2S_2O_8$, pyrrole, and PMMA concentration, and reaction time. The maximum conductivity value is 0.12 S/cm. The conductivity of the oxidized side is higher by over 1 order of magnitude than that of the evaporated side due to the localized distribution of polypyrrole perpendicularly to the film surface. The thickness of the films can be controlled by adjusting PMMA concentration. The practical lower limit of the film thickness, however, is of submicron order, because of decrease of the conductivity according to the defects in conducting paths of polypyrrole produced at too low a concentration of PMMA. The relationship between the transmittance and the logarithm of the conductivity gives a straight line with a gradient, ca. −8. The conductivity of the film is stable in dry state over 2000 h, but it decreases in the presence of the moisture by undoping of sulfate radical ions.

Nevertheless, the characteristic of this method enables one to prepare conducting thin films with desirable area, especially in large scale, easily and rapidly. It is expected that this method is practically effective for preparing the conducting composite thin films of polypyrrole by chemical polymerization.

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