Preparation of Conducting Polyacrylonitrile/Polypyrrole Composite Films by Electrochemical Synthesis and Their Electrical Properties

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SYNOPSIS

Electrically conducting polyacrylonitrile (PAN)/polypyrrole (PPy) composite films were prepared by electrochemical polymerization of pyrrole in an insulating PAN matrix under various polymerization conditions and their electrical properties were studied. The conductivities of PAN/PPy composite films peeled off from the platinum electrode lie in the range of 10^{-2}–10^{-3} s/cm, depending on the preparation conditions: The conductivity increased with the concentrations of the electrolyte and the monomer, but it decreased with the polymerization temperature of pyrrole and the applied potential.

INTRODUCTION

Electrically conducting polymers have excited considerable interest because many applications can be envisioned for electroactive materials. From the standpoint of technical applications, polypyrrole (PPy) is one of the most interesting conducting polymers because it is remarkably stable in ambient conditions and possesses high electrical conductivities.[1-10] The drawback of PPy is its poor mechanical properties, as in other conducting polymers. Improvements are expected from composite materials, where PPy furnishes the electrical and the matrix polymer furnishes the mechanical properties. PPy composites are synthesized by a chemical[11-13] or an electrochemical method.[14-16] The electrochemical approach has the advantage that the electrical properties of the composite can be changed simply by varying the electrolysis conditions in a controlled way.[17] Also, the electrochemical polymerization method eliminates the need of strong oxidizing agents and hazardous dopants. But the appropriate matrix polymer–electrolyte solution system, in which the matrix polymer swells and thus the ionic species such as the monomer and the electrolyte penetrate into it, should be available.

In this paper, we report studies on the electrical properties of conducting polyacrylonitrile (PAN)/PPy composites prepared for the first time by the electrochemical polymerization of pyrrole on the electrode coated with the PAN matrix film.

EXPERIMENTAL

Materials and Chemicals

PAN containing 12.1% of vinyl chloride as a comonomer was obtained as a commercial fiber grade and was purified twice with ethyl alcohol in a Soxhlet extractor. Pyrrole (Fluka) was stirred over CaH_2, distilled under vacuum before use, and stored under nitrogen atmosphere. Acetonitrile (Tedia) was also stirred over CaH_2 and then fractionally distilled under nitrogen atmosphere.

Commercially available ethylene glycol (Tokyokasei), dimethylformamide (DMF) (Duksan, phar.), lithium perchlorate ($LiClO_4$) (Aldrich), tetraethylammonium tetrafluoroborate (Et_4NBF_4) (Aldrich), tetramethylammonium hexafluorophosphate (Mt_4NPF_6) (Aldrich), and sodium p-toluenesulfonate (TsONa) (Tokyokasei) were used without further purification and electrolytes were dried at 70°C prior to use.
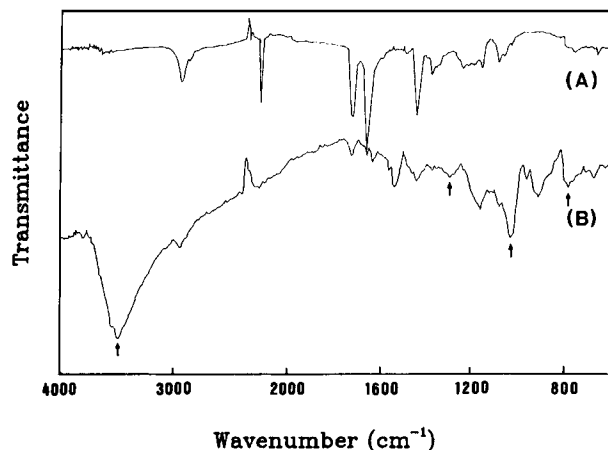
Figure 1 IR spectra of (A) PAN and (B) PAN/PPy composite prepared with Et₄NBF₄ as the electrolyte.

Preparation of PAN/PPy Composite Films

Electrochemical polymerization was carried out in a two-compartment cell of 30 mL capacity using a three-electrode system, i.e., a plate-typed Pt working electrode coated with ca. a 40 μm-thick PAN film (1.0 cm^2), a plate-typed Pt counter electrode (8.0 cm^2), and an aqueous sodium saturated calomel electrode (SSCE) as the reference. The potential in this work is with respect to SSCE. We also employed a Luggin capillary in order to reduce the uncompensated solution resistance between the working and reference electrode.[18] The working and counter electrodes were placed 2 cm apart.

The electrolyte solution consists of 30 mL acetonitrile (in the case of TsONa, the volume ratio of acetonitrile/ethylene glycol was 2 : 1), 0.1M pyrrole, and 0.1M supporting electrolyte. It was deaerated by bubbling nitrogen for 30 min. After bubbling, an inert atmosphere was assured successively by nitrogen flowing over the solution during polymerization.

Electrochemical syntheses of PAN/PPy composites were performed on EG & G PAR Model 173 Potentiostat connected to an EG & G PAR Model 179 coulometer. Potential was applied to the counter electrode by the constant potential-applying method. PAN/PPy composite film formed on the Pt electrode was rinsed thoroughly with acetonitrile, subsequently with purified water, and then peeled off from the electrode with a razor blade for the measurement of the electrical conductivity.

Measurement of Electrical Conductivity

The electrical conductivity of PAN/PPy composite films (if not otherwise indicated, the electrode side of the films) was measured at room temperature by the four-probe technique using an electrometer. The probe spacings (2 mm) were significantly greater than film thickness (40–80 μm), allowing the use of following equation:

$$\sigma = I \ln 2 / V\pi d$$

where σ is the conductivity (s/cm), d is the film thickness (in cm), and V/I is the sample resistance. Film thickness was measured with a profile projector (Mitutoyo, Type PJ-300). The details of experiments on measuring electrical conductivity have been described in our previous papers.[12,19]

Characterization of PAN/PPy Composite Films

The IR spectra were obtained using a Hitachi IR spectrophotometer (Model 260-30). Both the surface and the fracture surface of PAN/PPy composite films were observed using a Jeol JSM-35 CF electron microscope. The X-ray diffraction spectra were obtained using a Rigaku DMax IIIA wide-angle dif-

Table I   Electrical Conductivity and Average Current Density of PAN/PPy Composite Prepared with Various Electrolytes at the Constant Potential of 1.8 V and Consuming Charge of 360 mC/cm^2

Composite	Electrolyte	Average Current Density (mA/cm^2)	Conductivity (s/cm)
PAN/PPy	LiClO₄	100	1.64×10^{-2}
	Et₄NBF₄	440	2.21×10^{-2}
	Mt₄NPF₆	320	6.62×10^{-3}
	TsONa	180	4.41×10^{-3}

fractometer with Ni-filtered CuKα radiation. Thermogravimetric analysis measurements were made with a Perkin-Elmer thermogravimetric system TGA-7. The sample was heated at rate of 20°C/min in a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

The electrochemical polymerization of pyrrole on the PAN-coated Pt working electrode gave rise to black and flexible conducting composite films that can be peeled off from the electrode surface. These composite films are much easier to peel off and to handle than is pure PPy. To confirm the formation of PPy on the PAN matrix, the composite is characterized by IR spectra. Figure 1 represents the IR spectra of PAN and PAN/PPy composite film prepared with Et_4NBF_4 at the constant potential of 1.8 V and consuming charge of 360 mC/cm^2. From these spectra, it is apparent that PPy has been synthesized in the PAN matrix by the observation of the absorption bands at 3400–3200, 1290–1000, and 760–750 cm^{-1} assigned, respectively, to N—H stretching mode, C—H in-plane deformation vibration of an aromatic ring, and N—H wagging vibration, which are characteristic of PPy.

The electrical conductivity and average current density of PAN/PPy composite films prepared with various electrolytes are shown in Table I. The conductivities of composite films are in the range of 10^{-2}–10^{-3} s/cm, which are somewhat lower than those of PPy homogeneous films prepared with cor-
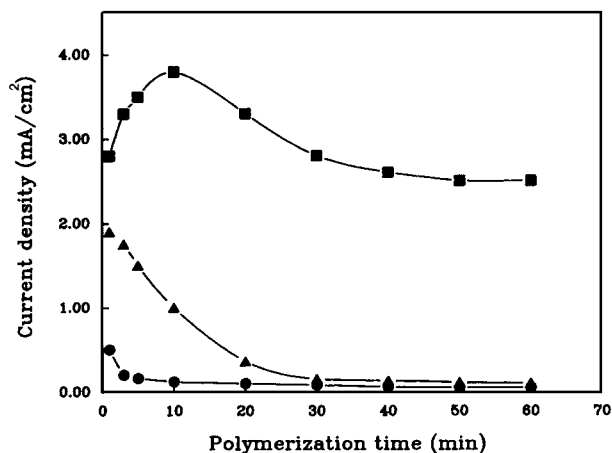
Figure 3 Dependence of current density on polymerization time of pyrrole and applied potential for the preparation of PAN/PPy composite films; (●) 2.1 V; (▲) 2.7 V; (■) 2.85 V vs. SSCE.

responding anions, ranging between 10^1 and 10^2 s/cm.[8] The conductivity of PAN homogeneous film is less than 10^{-14} s/cm, but PAN/PPy composite film with electrical conductivity as high as 2.21 × 10^{-2} s/cm has been obtained using Et_4NBF_4 as the electrolyte.

Figure 2 shows that conductivities of both sides, i.e., the electrode side and the solution side, of PAN/ PPy composite films prepared at the applied potential of 2.85 V depend on the polymerization time, which corresponds to the charge consumed during electrochemical polymerization of pyrrole. A few minutes later, after electrochemical polymerization started, the PAN film begins to darken, indicating that PPy is synthesized within the PAN matrix. Particularly, PPy grows rapidly through the thickness of the PAN film when the applied potential is higher than 2.85 V. When PPy is grown for more than 30 min at 2.85 V, both sides of the free-standing composite films are electrically conducting. However, if PPy is grown for a short time, for instance less than 30 min at the applied potential of 2.85 V or the applied potential is lower than 2.85 V, only the electrode side of composite film is electrically conducting, while the solution side remains insulating even after the fairly long time of PPy growth. Consequently, we can prepare the composite films that are electrically conducting on both sides or only on the electrode side by controlling the polymerization time and/or the applied potential for the electrochemical polymerization of pyrrole.

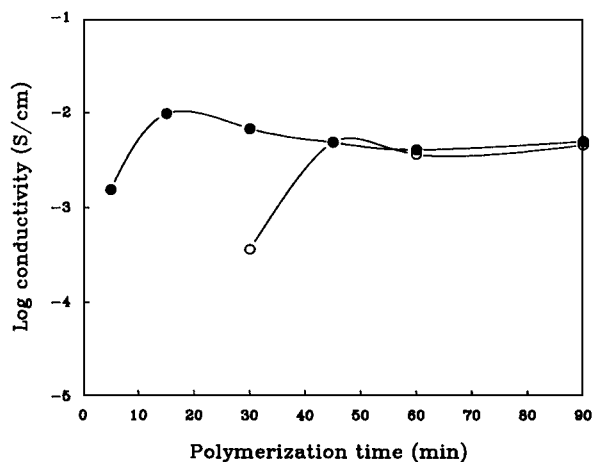It has been observed that the growth rate of PPy

Figure 2 Electrical conductivity of both sides of PAN/ PPy composite film as a function of polymerization time of pyrrole; (●) electrode side; (○) solution side.
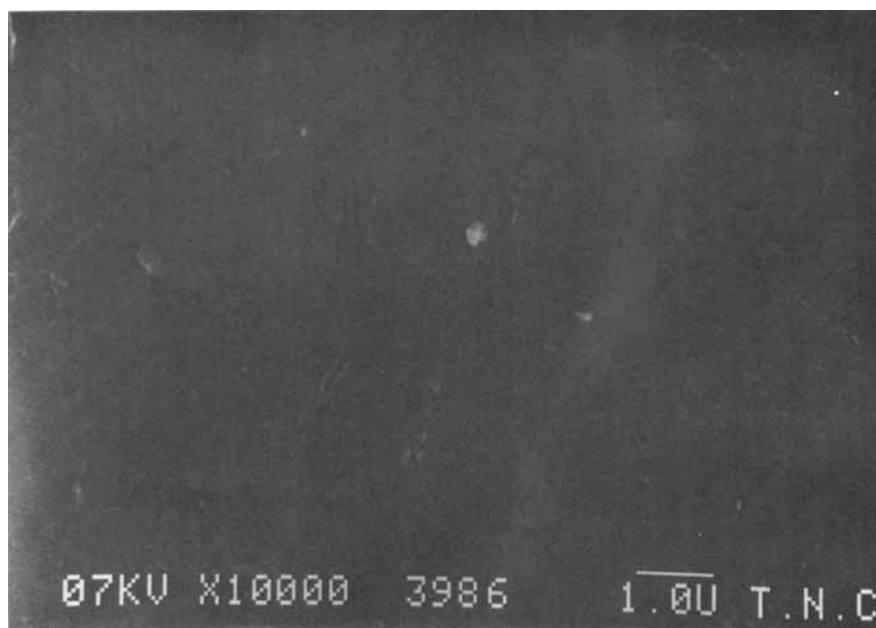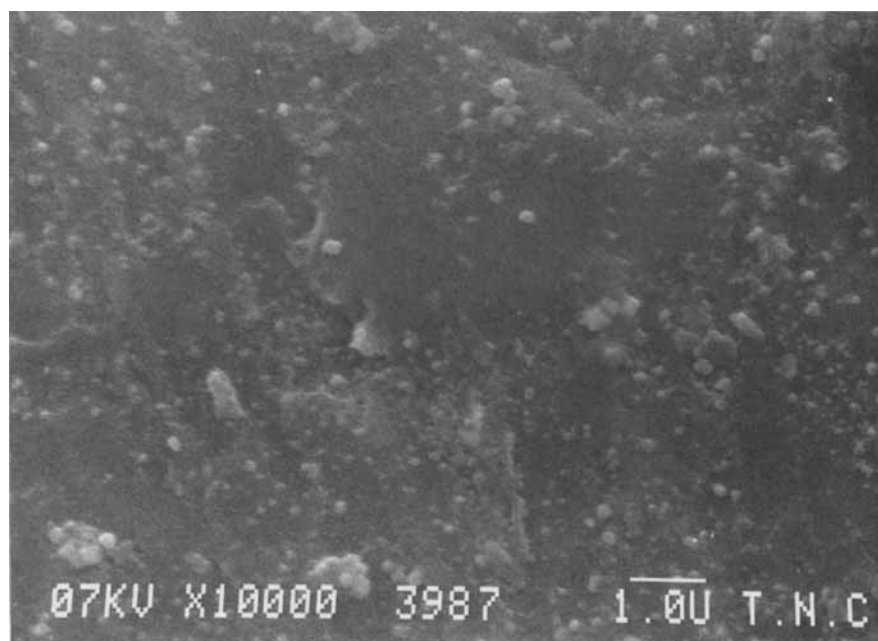
(A)

(B)

Figure 4   Scanning electron micrographs of solution side of PAN/PPy composite films; polymerization time of pyrrole: (A) 6 min; (B) 12 min; (C) 30 min; (D) 1 h; and (E) SEM of the cross section through the film thickness of the sample used in D.

depends on current density, which varies with the resistance of the electrolyte solution, the concentration of pyrrole, and the applied potential during the electrochemical polymerization.[20] Figure 3 shows the dependence of the current density on polymerization time of pyrrole and the applied potential for
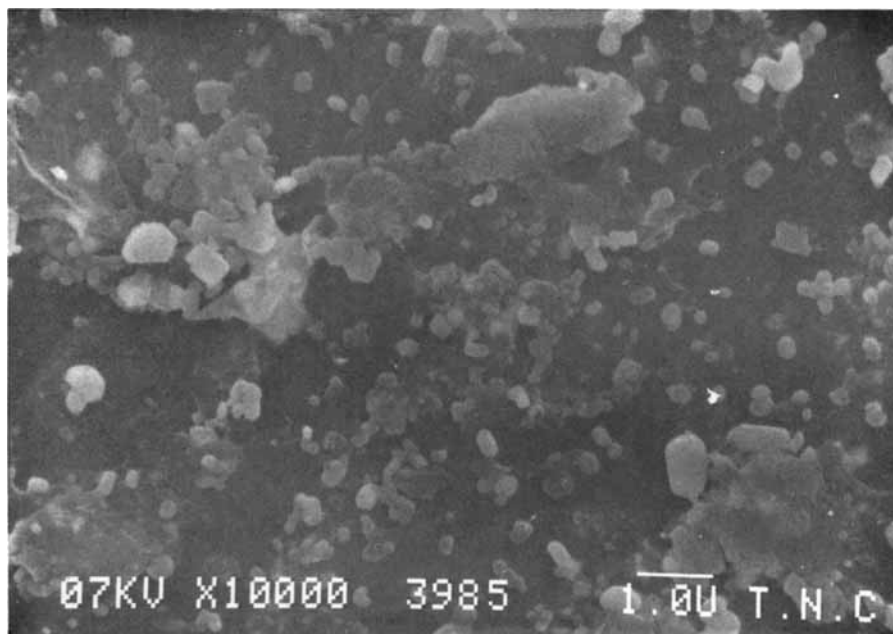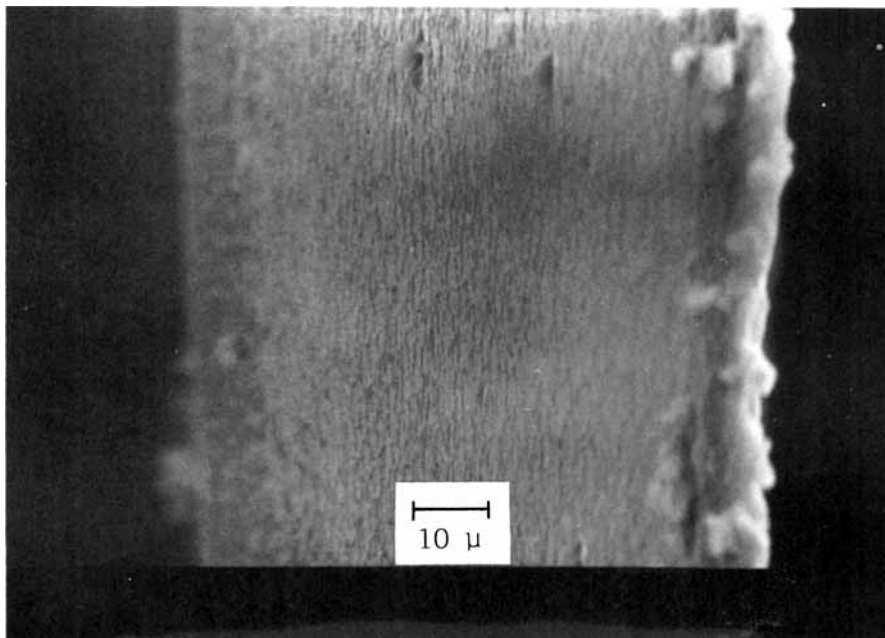
(C)
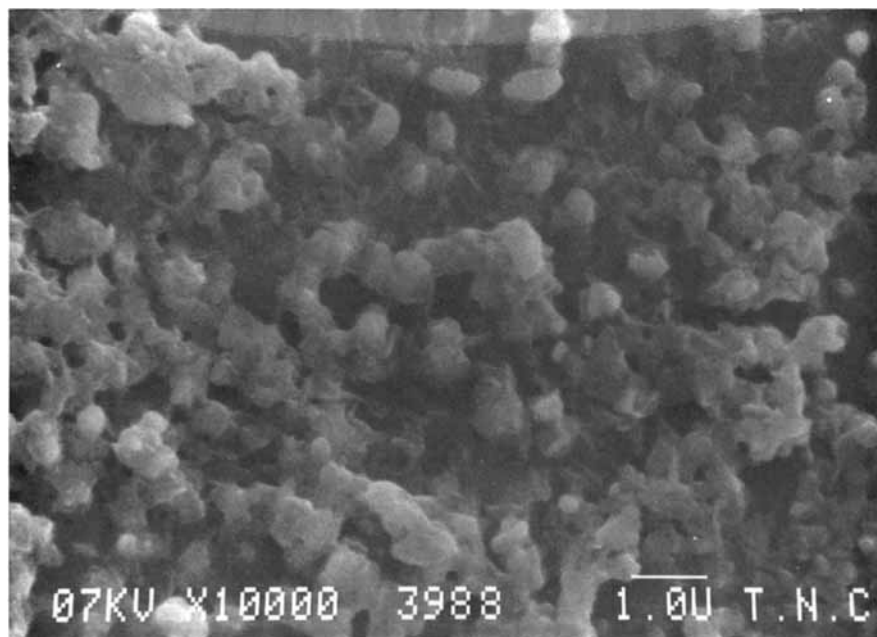
(D)

Figure 4   (*Continued from the previous page*)

the preparation of PAN/PPy composite films. Under the applied potential of 2.85 V, the current density increases with the polymerization time up to 10 min; thereafter, it decreases, and after 40 min, it has a constant value of around 2.5 mA/cm^2. This indicates that the pyrrole monomer and electrolyte

(E)

Figure 4   (*Continued from the previous page*)

penetrate into the swollen PAN film, reaching the surface of the Pt electrode, being polymerized on that, and the resulting PPy grows into PAN matrix to be completely conducting composite films within 40 min from the beginning of electrochemical polymerization of pyrrole. In contrast to this, the current density decreases continuously as electrochem-

ical polymerization proceeds when the applied potential is lower than 2.85 V, implying that synthesized PPy has not grown completely through the thickness of the PAN film. From this result, it is apparent that the growth rate of PPy in the PAN matrix is accelerated as the applied potential increases. The application of higher potential, how-
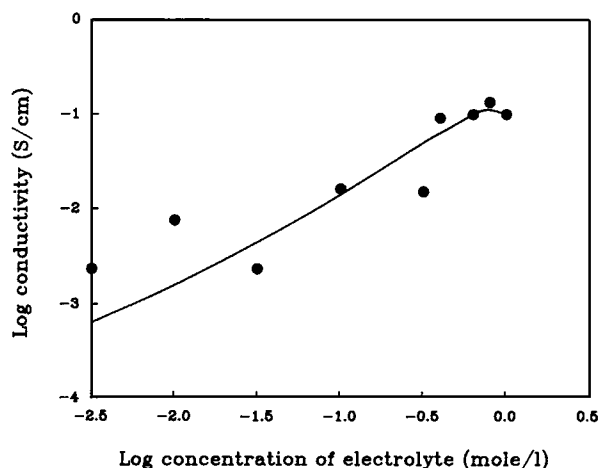

Figure 5   Dependence of electrical conductivity of PAN/PPy composite films on the concentration of the electrolyte, LiClO₄.
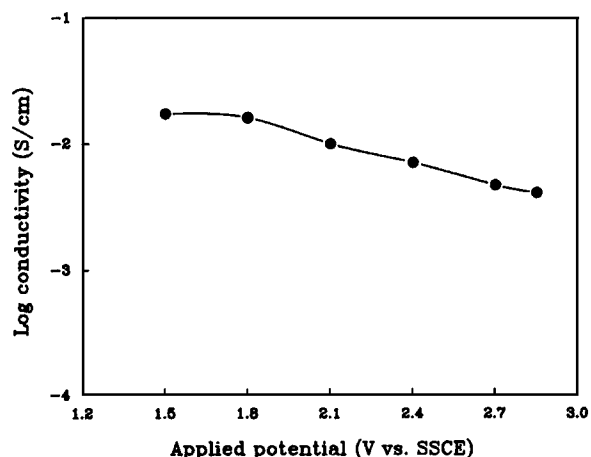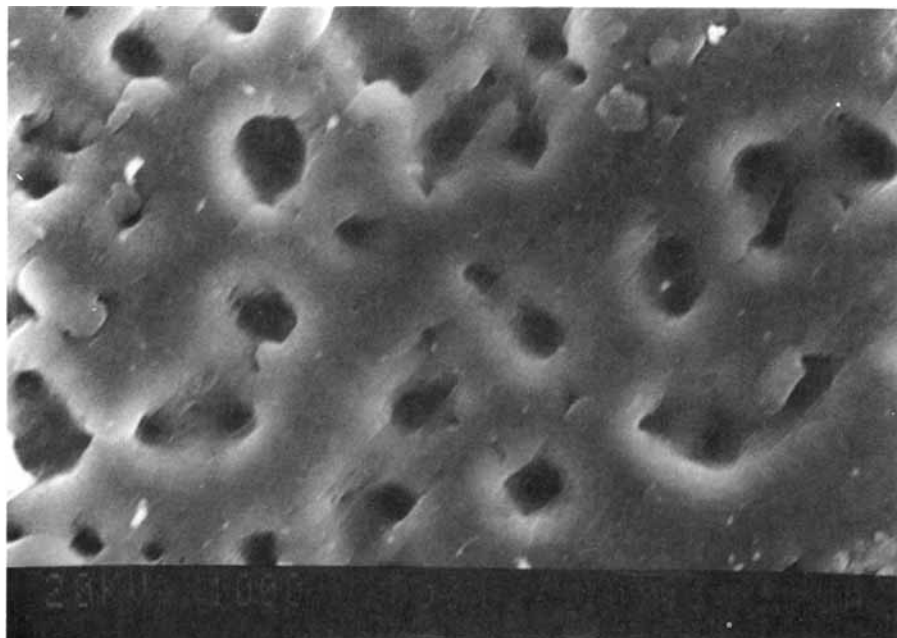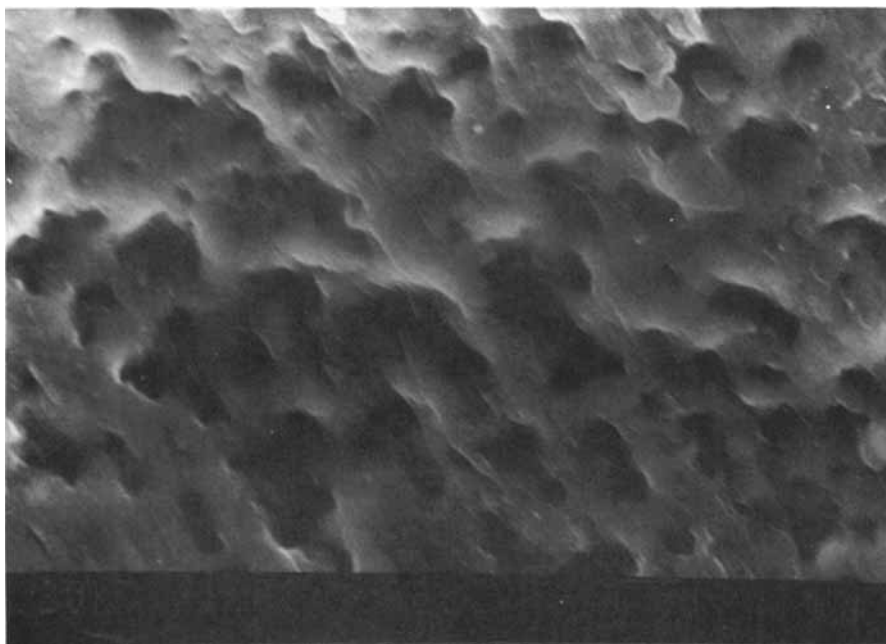

Figure 6   Dependence of electrical conductivity of PAN/PPy composite films on the applied potential during electrochemical polymerization.

(A)

(B)

Figure 7   Scanning electron micrographs of electrode side of PAN/PPy composite films prepared at different applied potential: (A) 1.5 V; (B) 2.1 V; (C) 2.7 V.

ever, may cause the discharge of the solvent–electrolyte system[21] or undesirable side reactions such as ring opening or breaking of conjugated system, which leads to an enhancement of defects and, con-

sequently, results in composite films of lower conductivity.[22]

To obtain information about the growth of the conducting PPy in the insulating PAN film, the
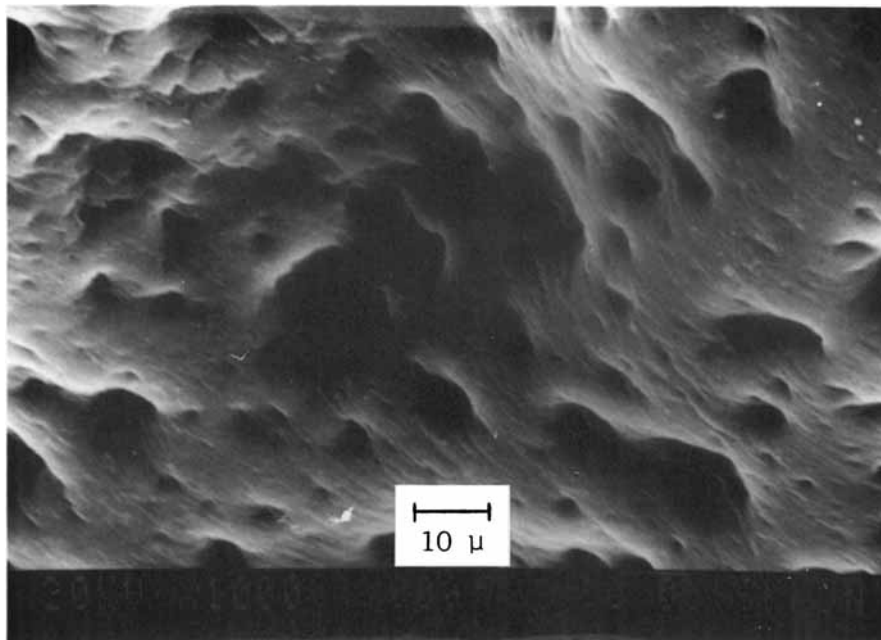
(C)

Figure 7 *(Continued from the previous page)*

scanning electron micrographs of the solution side of composite films have been taken (Fig. 4). The composite films were prepared by varying the electrochemical polymerization times at the constant applied potential of 2.85 V. As shown in Figure 4, PPy is formed as small granules at the early stage of polymerization and it grows successively to be connected to the continuous phase on the PAN matrix. Figure 4(E) shows the cross section through the film thickness of the sample used in Figure 4(D). The left side indicates the electrode side, and the right, the solution side. Thus, this represents clearly that if PPy is allowed to grow for sufficiently long periods of time, PPy is formed on the solution side as well as on the electrode side of composites.

Figure 5 shows the dependence of electrical conductivity of PAN/PPy composite films on the electrolyte concentration. The extended π-system in PPy films is oxidized electrochemically, being accompanied by the movement of the electrolyte anions into and out of the film to compensate the cationic charges in the oxidized PPy.[23] As shown in Figure 5, the electrical conductivity increases remarkably with the electrolyte concentration up to 0.8 mol/L (−0.1 mol/L in logarithmic scale), but it remains constant at higher concentration. This result implies that higher conductivity of the composite films prepared with higher electrolyte con-

centration stems from higher counteranion content and that the residual anions that existed in the solution are not included above that critical concentration of the electrolyte because PPy chains have ceased to grow. About one anion is contained for every three or four pyrrole unit in the PPy chain.[23,24]

Figure 6 shows the dependence of conductivity of PAN/PPy composite films on the applied potential during the electrochemical polymerization. The
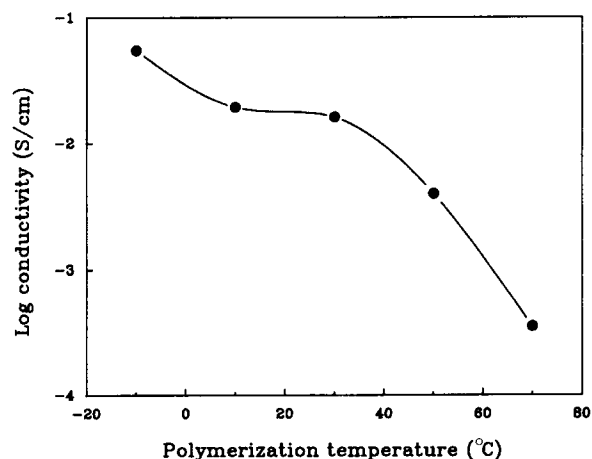

Figure 8 Dependence of electrical conductivity of PAN/PPy composite films on the temperature of electrochemical polymerization.
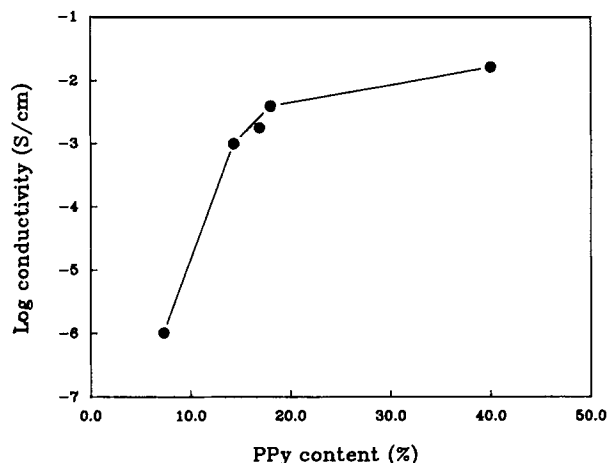
Figure 9 Dependence of electrical conductivity of PAN/ PPy composite films on PPy content in composite.

conductivity decreases with the increase of the applied potential. Higher conductivity of the composite films prepared at a lower applied potential might be related to better morphology—longer conjugation length with fewer defects, which is needed for better electrical conduction. Figure 7 shows the SEMs of PAN/PPy composite films prepared by varying the applied potential during the electrochemical polymerization. The surface of the composite film prepared at a lower applied potential is smoother and more uniform, but it becomes rougher and nonuniform as the applied potential increases. Unfortunately, we have failed to prepare PAN/PPy composite films at potential lower than 1.5 V.

We have also investigated the effect of the polymerization temperature on the conductivity of PAN/PPy composite films. As shown in Figure 8, higher conductivity has been obtained at lower polymerization temperature. We are inclined to attribute this result to the morphology and the side reaction, which result in lower conductivity by the higher temperature of electrochemical polymerization.

In Figure 9, the conductivity of PAN/PPy composite films is plotted as a function of PPy content in composite. The weight fraction of PPy in PAN/ PPy composites was determined by weighing PAN-coated electrode prior to and subsequent to electrochemical polymerization. The amounts of PPy in the composite was varied by changing the electrochemical polymerization time. It is found that the conductivity is proportional to the weight fraction of PPy in the composite, as indicated in Figure 9. The composite film shows a steep increase in con-

ductivity up to 14.3 wt % of PPy content in the composites and finally shows the saturation value of the conductivity, implying that PPy forms its own conducting paths and bridges for charge transport in the PAN matrix and electrode interface, which led to the surface conduction.

The thermal gravimetric analyses (TGA) of pure PAN and PAN/PPy composite films in a nitrogen atmosphere are shown in Figure 10. Both films show a weight loss at around 255°C and then begin to lose their weight rapidly above that temperature, increasing to 10% at 330°C, as indicated in Figure 10. PAN/PPy composite films are more stable than is pure PAN film. By comparison, PAN/PPy composite and pure PAN films lose their weight by 38.5% and 53.5%, respectively, when heated up to 600°C.

Figure 11 shows the X-ray diffraction spectra of PAN and PAN/PPy composite films. The intense crystalline peak of PAN appeared at $2\theta = 16.8°$, but its intensity decreased considerably by the formation of PPy in PAN/PPy composite. Based upon these observed X-ray diffraction scans, it is apparent that crystallinity of PAN decreases by the electrochemical polymerization of pyrrole in the PAN matrix.

CONCLUSION

In conclusion, we have found that the formation of PPy in the PAN matrix films by the electrochemical polymerization method can be confirmed by IR spectroscopy and scanning electron microscopy. The electrical properties of the obtained PAN/PPy composite films are influenced by the preparation conditions such as the kind and the concentration
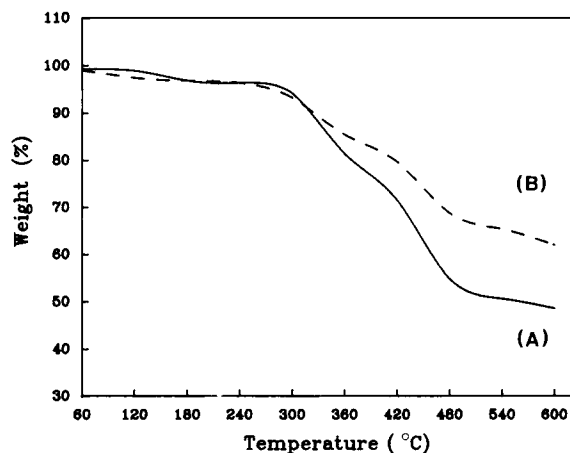

Figure 10 Thermal gravimetric analysis of (A) PAN and (B) PAN/PPy composite films.
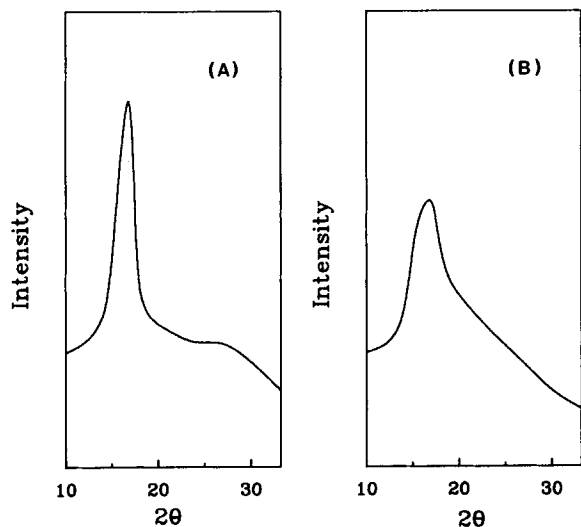
Figure 11   X-ray diffraction curves of (A) PAN and (B) PAN/PPy composite films.

of the electrolyte, the applied potential, and the polymerization temperature, which are also related to the different morphologies of the composites. The TGA result shows that PAN/PPy composite film is more stable with temperature than is pure PAN. The X-ray diffraction result shows that the crystallinity of PAN decreases by the formation of PPy in the PAN matrix.

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