Ionic Interactions in Polyacrylonitrile/Polypyrrole Conducting Polymer Composite

YOUNGKWAN LEE,[1] DONGKI SHIN,[1] JAECHOON CHO,[1] YUN HEUM PARK,[2] YONGKEUN SON,[3] DOO HYUN BAIK[4]

[1] Department of Chemical Engineering, Sung Kyun Kwan University, Suwon 440-746, South Korea

[2] Department of Textile Engineering, Sung Kyun Kwan University, Suwon 440-746, South Korea

[3] Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, South Korea

[4] Department of Textile Engineering, Chungnam National University, Daejeon 305-764, South Korea

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ABSTRACT: A conducting polymer composite was prepared by the postpolymerization of pyrrole in a polyacrylonitrile (PAN) matrix film. To enhance the electrostatic interaction between the two phases, a small amount of a sulfonate (SO_3^-) or a carboxylate (COO^-) group was incorporated into the PAN structure. The presence of electrostatic interaction between the conducting polypyrrole and the anion-containing PAN copolymer was elucidated by examination of the morphology and the electrical properties of the composite. The aromatic sulfonate-containing matrix provided the composite with the best results in the electrical conductivity, the environmental stability of conductivity, and the morphological property. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2641–2648, 1998

Key words: conducting polymer composite; polyacrylonitrile; polypyrrole; electrostatic interaction

INTRODUCTION

Conducting polymers exhibit excellent electrical properties; however, the common usage of this material has been restricted due to the poor processability and the lack of stability.[1] Various techniques, such as the modification of the monomer structure,[2,3] the utilization of a soluble precursor,[4] and the formation of a blend or composite,[5–8] have been introduced to enhance the processability. The composite formation is one of the simplest methods for providing the processability of a conducting polymer. However, a conducting polymer exhibits poor compatibility with common polymers due to the chain rigidity originated from an extended conjugate double bond. In the case of a conducting composite prepared by the simple coating of conducting polymers onto the surface of the matrix polymer, any interaction between the two components usually does not exist and the conducting polymer can be easily removed from the matrix polymer by repeated friction to result in the ultimate failure of the electrical property. In this regard, it should be stressed that the interaction between the two components should exist in order to provide the desirable properties.

The utilization of an anion-containing polymer as a matrix material is based on the scenario of introducing an electrostatic interaction with a

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Correspondence to: Y. Lee.

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cation-carrying conducting polymer in the doped state. Various water-soluble polyelectrolytes have been used in a conducting composite as a matrix material by an electrochemical polymerization technique.[9–12] In this case, a matrix polymer can act as a polymeric dopant. The ionic interaction between the two components allows the uniform dispersion of the conducting polymer into the matrix as well as the higher stability of the electrical conductivity. It has been known that the decrease in the conductivity is due to the volatilization of a mineral dopant ion from the conducting polymer.[13] In this regard, the advantages of the polymeric dopant system would provide the composite with better electrical properties as well as long-term stability.

In this study, a conducting composite was prepared by postpolymerization of pyrrole into the PAN matrix film. PAN is generally used in textile applications owing to the good mechanical and thermal properties as well as a relatively cheap price. The structure of the PAN was modified to incorporate a small amount of anionic moieties by the copolymerization of acrylonitrile with acrylic acid or styrene sulfonate. The copolymer containing acrylic acid was converted to an anionic form by the reaction with a metal hydroxide base. The conducting polymer composite was prepared by polymerizing pyrrole into the matrix film. The effect of ionic groups in the matrix on the conducting composite formation was examined in terms of the morphological, electrical, and thermal properties. The environmental stability of the electrical conductivity was also monitored as a function of time and temperature. This composite preparation technique can be utilized in the manufacturing of high-performance conducting textile materials.

SAMPLE PREPARATION AND EXPERIMENTAL

Reagents

Acrylonitrile (Junsei, Tokyo, Japan), acrylic acid (Junsei), and pyrrole (Aldrich, Seoul, Korea) were freshly distilled before use. Sodium styrene sulfonate (Aldrich), acetonitrile (Junsei), and ferric chloride (Aldrich) were used as received.

Synthesis of PAN Copolymer

The PAN copolymers were designed to have a small amount of carboxylate groups or sulfonate groups, and copolymerization was carried out using acrylic acid or styrene sulfonate as a comonomer. PAN and PAN copolymers were synthesized by the redox polymerization technique.[14] Polymerization was carried out with various compositions of the monomer feed in the water medium at 40°C for 2 h using a $K_2S_2O_8$/$NaHSO_3$ initiator system. The polymer obtained from a reaction medium was filtered and rinsed with methanol and water several times to remove unreacted monomers as well as water-soluble homopolymers. The purified polymers were dried in a vacuum at 50°C for 24 h.

Conducting Composite Formation

The conducting composite films were prepared as follows: Thin films of the matrix polymer with a thickness of 20–50 μm were prepared by solution casting using the DMF or DMSO solvents for poly(acrylonitrile-*co*-acrylic acid) (PAN-*co*-PAA) and poly(acrylonitrile-*co*-sodiumstyrenesulfonate) (PAN-*co*-PSS), respectively. For the preparation of the matrix film, the polymer was dissolved in the desired solvent (5 wt %) and a few drops of the solution was poured onto a glass plate and dried at 60°C for 24 h in a vacuum. The matrix films thus cast were immersed in the pyrrole monomer solution (acetonitrile/pyrrole/water: 70/20/10, v/v/v) for the required time in order to impregnate pyrrole into the matrix. The film was taken out of the pyrrole solution, washed with deionized water several times, and transferred to 100 mL of an aqueous $FeCl_3$ oxidant solution (0.1*M*) for the polymerization. The polymerization of pyrrole in the matrix film took 30 min. The resulting conducting composite film was rinsed with water several times and dried in a vacuum at 40°C for 24 h for the characterization.

Characterization

The chemical structure of the PAN copolymer was examined by a Mattson 1000 FTIR. The thermal properties were measured by a Perkin–Elmer TGA 7. The ion contents of the PAN copolymer were measured using an acid/base titration method, a Hitachi Z-600 atomic absorption spectrophotometer, and a Leco elemental analyzer. The morphology of the composite films was monitored by a Hitachi S-2400 scanning electron microscope. The electrical conductivity of the composite film was measured by a four-in-line parallel probe method with a constant weight contact using a Keithley 236 source measure unit.

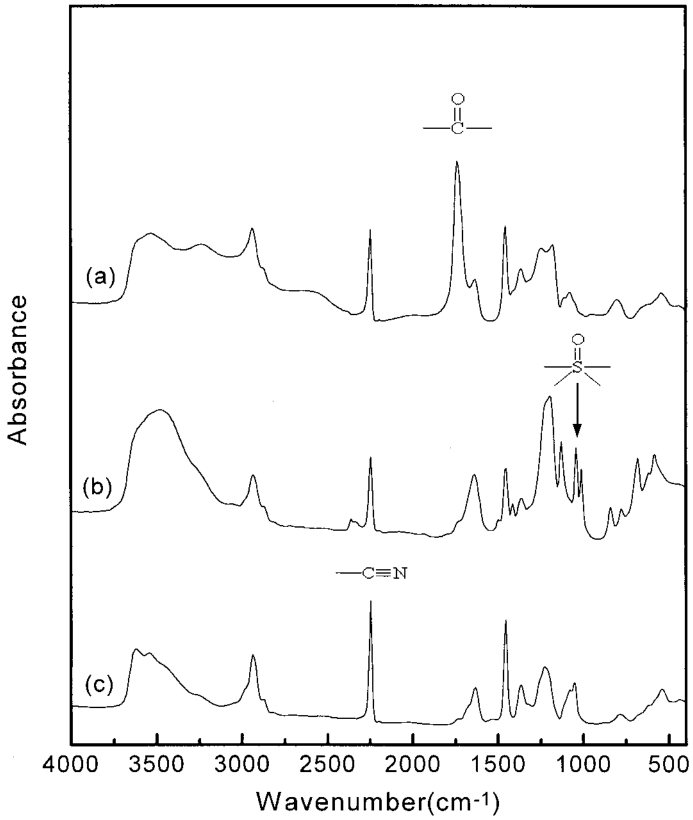


Figure 1 FTIR spectra of (a) PAN-*co*-PAA, (b) PAN-*co*-PSS, and (c) PAN.

RESULTS AND DISCUSSION

Synthesis of PAN and Copolymers

PAN and PAN copolymers were synthesized by the redox polymerization technique. The structure of the polymers, PAN-*co*-PAA and PAN-*co*-PSS, was examined by FTIR, as shown in Figure 1. An absorption band at 2240 cm^{-1} is assigned to nitrile (C≡N) stretching from PAN. In the copolymers, new absorption bands appeared (a) at 1730 and (b) at 1046 cm^{-1}, which correspond to a carbonyl (C=O) stretching and a sulfonate (S=O) stretching mode, respectively. This indicates the successful incorporation of acrylic acid or the styrene sulfonate group into the copolymer structure. The acrylic acid is easily converted to the ionic form by neutralization with a metal hydroxide solution. The amount of acrylic acid and styrene sulfonate in the copolymer was quantitatively measured by acid/base titration, an atomic absorption spectrophotomer, and elemental analysis. It was observed that 3.5–13 mol % of the acrylic acid and 4–11 mol % of the styrene sulfonate were incorporated into the copolymer structure depending on the monomer feed. The compositions of the copolymer with various monomer feeds are shown in Table I. The intrinsic viscosities of the copolymers were measured using the DMF and DMSO solvents for PAN-*co*-PAA and PAN-*co*-PSS, respectively. The molecular weights of the PAN-*co*-PAA copolymers were calculated by a solution viscosity measurement using the DMF solvent, suggested by Kobayashi as follows.[15] In case of the PAN-*co*-PSS, the molecular weight was not obtained due to the insolubility in DMF and Mark–Howink constants for the DMSO solvent are not available in the literature:

$$[\eta](\mathrm{dL/g}) = 2.78 \times 10^{-4} M^{0.76}$$

Physical Properties of PAN Copolymers

The thermal stability of PAN and PAN copolymers was examined by TGA in a N_2 atmosphere and the thermograms are shown in Figure 2. The onset point of the thermal degradation appears at 300, 280, and 360°C for PAN, PAN-*co*-PAA, and PAN-*co*-PSS, respectively. The changes of the

Table I Polymerization Data

Polymer	PAN	PAN-*co*-PAA (3.5)	PAN-*co*-PAA (6.2)	PAN-*co*-PAA (8.9)	PAN-*co*-PAA (12.8)	PAN-*co*-PSS (3.9)	PAN-*co*-PSS (4.2)	PAN-*co*-PSS (8.1)	PAN-*co*-PSS (10.8)
Comonomer content in the monomer feed (mol %) M_2	—	3	6	9	15	5	10	15	20
Comonomer content in the copolymer (mol %) m_2	—	3.5	6.2	8.9	12.8	3.9	4.2	8.1	10.8
$(m_2/M_2) \times 100$	—	117	103	99	85	78	42	54	54
Yield (%)	90	90	84	89	75	80	49	48	37
Intrinsic viscosity (dL/g)	3.12[a]	2.65[a]	3.93[a]	4.86[a]	3.69[a]	20.8[b]	10.1[b]	7.07[b]	3.84[b]
$M_w \times 10^{-4}$	21.3	17.2	28.9	38.2	26.6	—	—	—	—

[a] Viscosity measured in DMF.

[b] Viscosity measured in DMSO.

thermal stability might be due to the incorporation of comonomers having different thermal stability. It is generally accepted that acrylic acid induces decarboxylation at elevated temperature and the aromatic styrene sulfonate groups result in higher thermal stability.

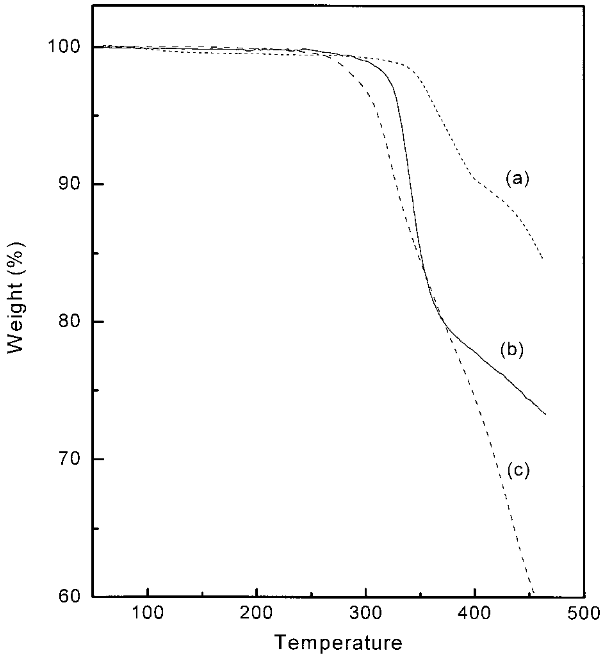


Figure 2 TGA thermograms of (a) PAN-*co*-PSS, (b) PAN, and (c) PAN-*co*-PAA.

The incorporation of a small amount of polar ionic groups into the PAN structure also resulted in a solubility change, as shown in Table II. The solubility of PAN-*co*-PAA is similar to that of PAN; however, PAN-*co*-PSS shows limited solubility in DMAc and DMF. This might be due to the stronger ionic association of sulfonate groups than of carboxylate groups. The presence of ionic groups in both copolymers induces swelling behavior in water, which results in the morphology change of the matrix film. The significance of the morphology change for the preparation of the con-

Table II Solubilities of PAN, PAN-*co*-PAA (8.9 mol %), and PAN-*co*-PSS (8.1 mol %)

Solvent	PAN	PAN-*co*-PAA	PAN-*co*-PSS
Acetone	×	×	×
Acetonitrile	×	×	×
Benzene	×	×	×
Chloroform	×	×	×
m-Cresol	×	△	○
DMAc	○	○	△
DMF	○	○	△
DMSO	○	○	○
Ethanol	×	×	×
Methanol	×	×	×
THF	×	×	×
Water	×	△	△

(○) Soluble; (△) swell; (×) insoluble.

ducting composite with desirable properties will be discussed in detail. It seems that the morphology change allows pyrrole impregnation into the matrix.

Preparation and Physical Properties of Conducting Composites

The composite formation is achieved in two steps: impregnation of the matrix film with a pyrrole monomer followed by the polymerization of pyrrole in the matrix using $FeCl_3$ as an oxidant. To incorporate the pyrrole monomer into the matrix film, several solution systems were examined. In the case that the matrix films are immersed in pure pyrrole or organic solutions of pyrrole, such as acetonitrile or an alcohol solution, the pyrrole monomer is not impregnated into the matrix at all and, consequently, the desirable conducting composite films are not obtained. As discussed previously, the ionic groups in the copolymer cause swelling in water, resulting in the morphology change. To incorporate the pyrrole monomer into the matrix, a mixed solution system was employed. The best solution system for pyrrole impregnation was the mixed solution having a small amount of water (acetonitrile/pyrrole/water: 70/20/10, v/v/v). In the case of the unmodified PAN matrix, it takes a much longer time for pyrrole impregnation. It is conceivably due to the compact morphology of the matrix film which does not allow pyrrole impregnation.

As soon as the matrix films containing the pyrrole monomer make contact with the oxidant solution, polymerization occurs immediately and the films turn black. So, the impregnation of the matrix with the pyrrole monomer is the key step in order to control the electrical conductivity of the composite film. In our experiment, the polymerization time has been concluded to be 30 min to allow complete polymerization of pyrrole in the matrix. The formation of a conducting composite was confirmed by FTIR and UV spectroscopy and their spectra are shown in Figure 3. The appearance of an absorption band at the high-frequency region in the FTIR spectrum indicates the metallic character of the conducting composite. In the UV spectrum, a broad charge carrier band also appears in the low-energy region.

To obtain detailed information of the dopant composition, the composite film was analyzed by energy-dispersive spectroscopy. The relative amount of Fe and Cl is shown in Table III. The amount of Cl is reduced in the copolymer/polypyrrole (PPy) composite, which obviously indicates that the polymeric anion functions as a polymeric dopant. The morphology of the composite film was investigated by scanning electron microscopy, as shown in Figure 4. The PPy domains from the surface of PAN and the PAN–copolymer matrix films can be seen. The PAN/PPy composite shows the large aggregate of PPy, exhibiting a distinct phase separation. However, the copolymer/PPy composites exhibit regularly dispersed fine particles of PPy. This is possibly due to the ionic interaction between the anion-containing matrix and the cation-containing PPy. In the case of the PAN/PPy composite, any interaction between the two components does not exist and the PPy domains are easily formed. However, in the case of the anion-containing copolymer/PPy composite, ionic interaction exists between them, which induces regular dispersion of PPy on the matrix as well as a higher adhesive strength between them.

The electrical conductivity of the PAN-*co*-PAA/PPy and the PAN-*co*-PSS/PPy composite films compared with homo-PAN is shown in Figures 5 and 6, respectively. The electrical conductivity was monitored as a function of pyrrole impregnation time. In the PAN-*co*-PAA/PPy composite system, the conductivity increased to $\sim 7 \times 10^{-2}$ s/cm after 1 min of impregnation time. In the case of the PAN-*co*-PSS/PPy composite system, the conductivity increased to $\sim 5 \times 10^{-1}$ s/cm within 4–8 min depending on the matrix structure. It is found that the ion content in the matrix film does not affect the electrical conductivity significantly. It can be seen that the increase of conductivity is closely related to the increase of the PPy content. The PPy content was calculated by the weight increase after composite formation. In case of the PAN/PPy composite film, it takes a much longer period of time for pyrrole impregnation and the conductivity of the resulting film is much lower than that of anion-containing copolymer/PPy composite. As discussed previously, pyrrole is easily impregnated into the matrix from the water-containing solution; however, the PAN homopolymer does not have any affinity for water or for the pyrrole monomer. This might cause the lower conductivity for the PAN/PPy composite as well as the longer time scale for the composite preparation.

The electrical conductivity of the composite at elevated temperature was also examined in order to evaluate the environmental stability of the conducting composite. The conductivity decreases as a function of time as shown in Figure 7. It has

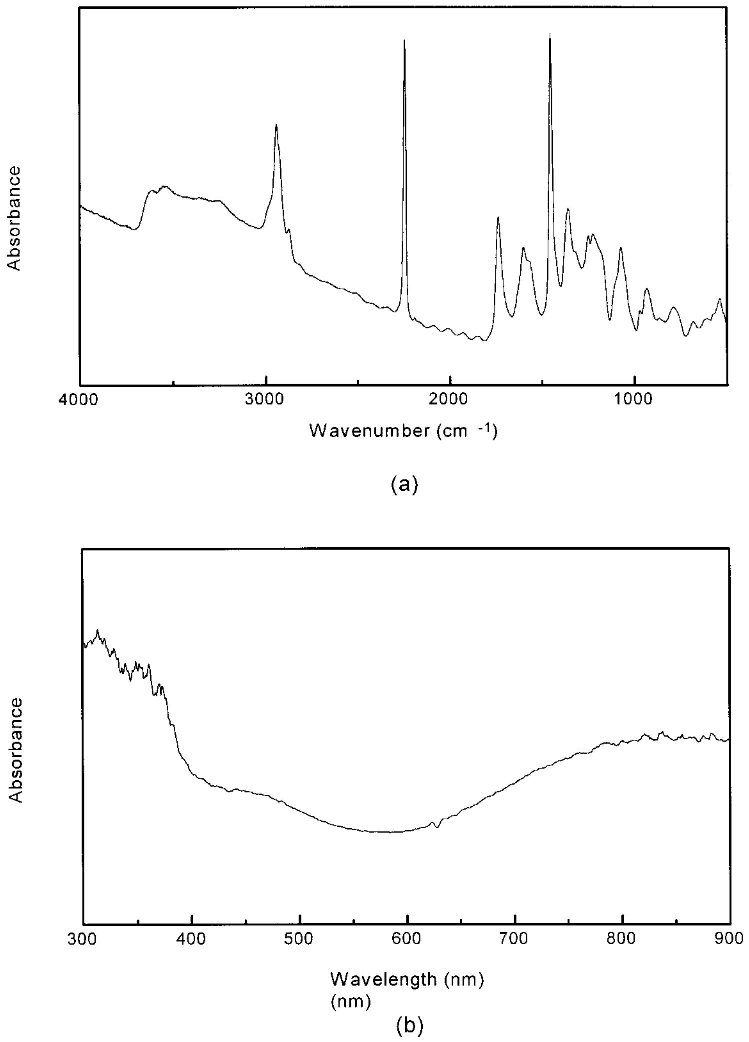
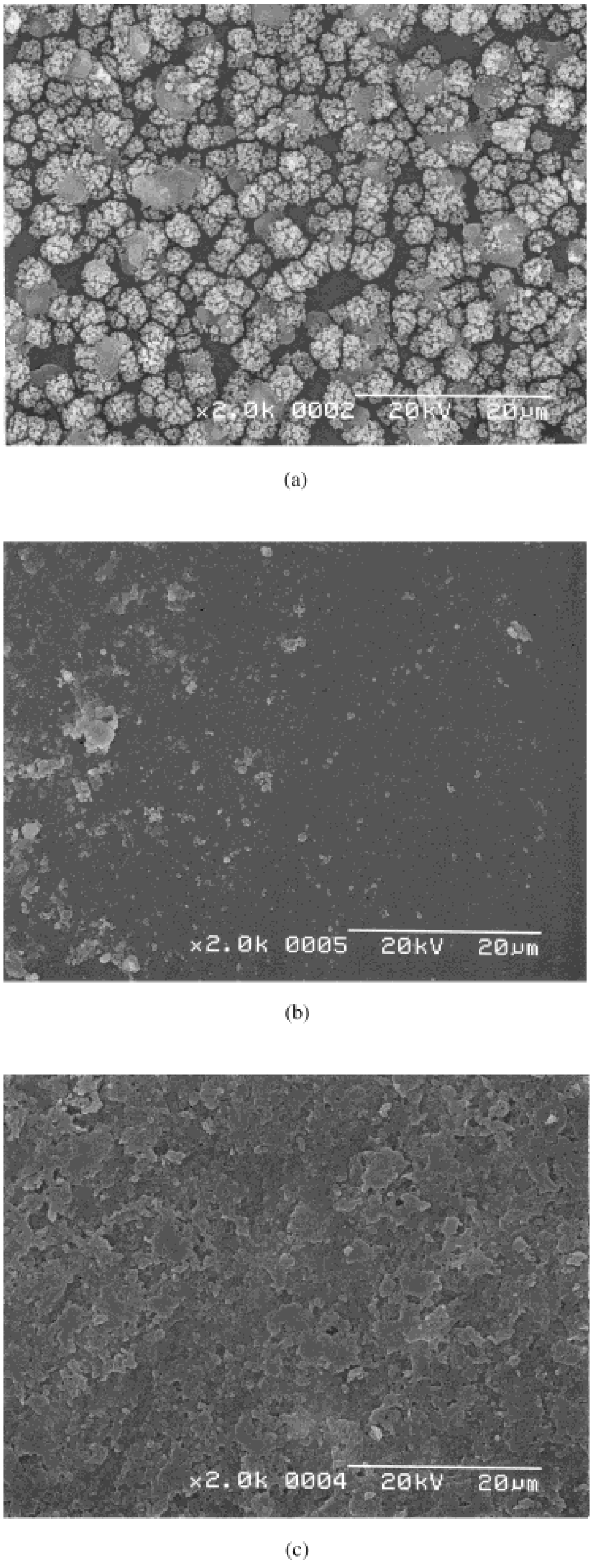


Figure 3 (a) FTIR and (b) UV-vis spectra of PAN-*co*-PAA/PPy composite.

been known that the conductivity decrease of PPy doped with mineral anions is related to an instability of these species either with respect to the polymer chain or to their volatillization.[13] It can be seen that the conductivity decreases much faster at higher temperature which might be due to the faster volatillization of the dopant anion. To examine the effect of the matrix nature on the electrical property and the stability, three different matrix films were used for the composite preparation, such as homo-PAN, PAN-*co*-PAA, and PAN-*co*-PSS. The carboxylate containing PAN-*co*-PAA does not exhibit any improvement in the stability, which might be due to the fact that

Table III Energy-dispersive Spectroscopy for PAN/PPy Composite, PAN-*co*-PAA/PPy Composite, and PAN-*co*-PSS/PPy Composite

Specimen Composition	PAN/PPy Composite (mol %)	PAN-*co*-PAA/PPy Composite (mol %)	PAN-*co*-PSS/PPy Composite (mol %)
Fe	22%	34%	40%
Cl	78%	66%	60%
Fe/anion	1/3.5	1/1.9	1/1.5



(a)

(b)

(c)

Figure 4 SEM images of (a) PAN/PPy composite, (b) PAN-*co*-PAA/PPy composite, and (c) PAN-*co*-PSS/PPy composite.

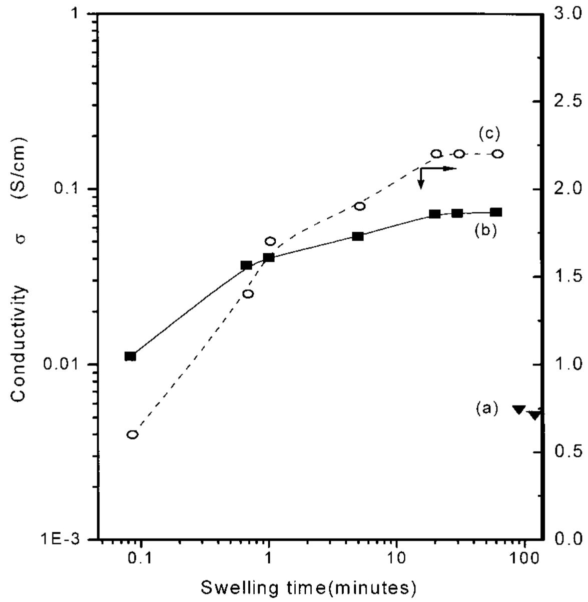


Figure 5 Conductivity of PAN-*co*-PAA/PPy composites containing (a) (▼) 0 mol % and (b) (■) 8.9 mol % of ion content and (c) PPy content of the composite containing (○) 8.9 mol % of ion content.

decarboxylation occurs at elevated temperature. It is also clearly seen that aromatic sulfonate containing PAN-*co*-PSS exhibits much higher sta-

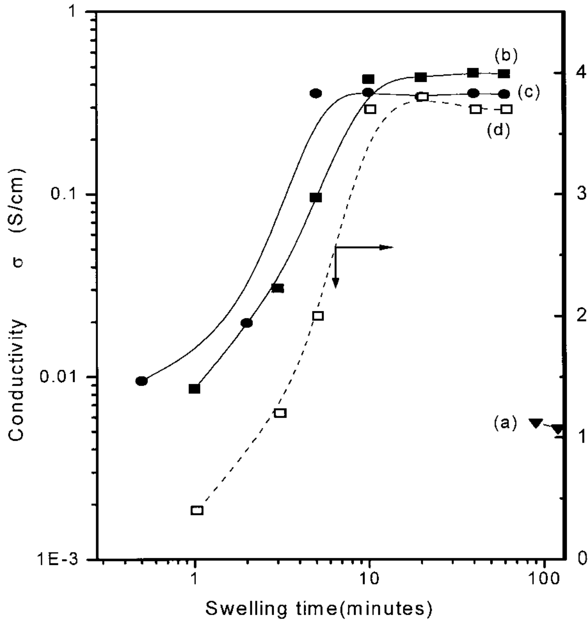


Figure 6 Conductivity of PAN-*co*-PSS/PPy composites containing (a) (▼) 0 mol %, (b) (■) 4.2 mol %, and (c) (●) 10.8 mol % of ion content and (d) (□) PPy content of the composite containing 4.2 mol % of ion content.

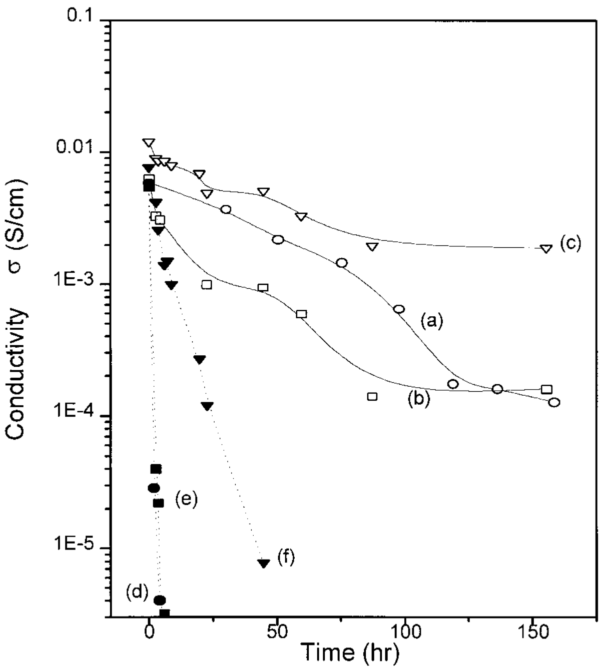


Figure 7 Stability of the electrical conductivity of the composites at 70°C: (a) (○) homo-PAN, (b) (□) PAN-*co*-PAA 3.5 mol %, and (c) (▽) PAN-*co*-PSS 3.9 mol % stability at 130°C; (d) (●) homo-PAN; (e) (■) PAN-*co*-PAA 3.5 mol %; (f) (▼) PAN-*co*-PSS 3.9 mol %.

bility than that of the others. This might be attributed to the high stability of polymeric aromatic sulfonate-doped PPy with respect to volatillization, decomposition, or chemical reactivity.

CONCLUSIONS

Conducting polymer composites of PAN/PPy were prepared by the impregnation of pyrrole into the matrix followed by the polymerization of pyrrole in the matrix film. A small amount of anions was incorporated into the PAN structure. In the composite preparation, a mixed solution of pyrrole was used for the pyrrole impregnation. The incorporation of anionic moieties on the matrix film causes the electrostatic interaction between the conducting PPy in the doped state. The electrostatic interaction between the two components resulted in the better morphological and electrical properties of the composite film. In this study, an aromatic sulfonate-containing polymer matrix results in the most desirable physical properties on the conducting composite.

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