

Potassium Persulfate-Mediated Preparation of Conducting Polypyrrole/Polyacrylonitrile Composite Fibers: Humidity and Temperature-Sensing Properties

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ABSTRACT: Conducting polypyrrole (PPy)/polyacrylonitrile (PAN) composite fibers were prepared by the polymerization of pyrrole in the presence of PAN fibers with potassium persulfate in an acidic aqueous solution. We obtained composite fibers containing concentrations of PPy as high as 1.14% and having surface resistivities as low as $0.6 \text{ k}\Omega/\text{cm}^2$ by changing the polymerization parameters, including the temperature and concentrations of pyrrole and oxidant. The tensile strength of 10.02 N/m^2 and breaking elongation of 32.68% for the pure PAN fiber increased up to 10.45 N/m^2 and 33.23%, respectively, for the composite fiber containing 0.13% PPy. The change in the resistivity

of the PPy/PAN composite fiber during heating-cooling cycles in the temperature range of $+5$ to 120°C was examined. Scanning electron microscopy and optical microscopy images of the composite fibers showed that the PPy coating was restricted to the surfaces of the PAN fibers. Surface resistivity measurements, Fourier transform infrared spectroscopy, and thermogravimetric analysis techniques were also used to characterize the composite fibers. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; conducting polymers; fibers; polypyrroles; sensors

INTRODUCTION

Conducting fibers have recently attracted considerable interests because of their potential for being used in technological areas, such as electromagnetic interference shielding,¹ rechargeable batteries,² and deelectrifying applications.³ Therefore, studies on the preparation of conducting fibers are frequently encountered in the literature.

There are various successful approaches for preparing conducting fibers. One of them is the spinning of the conducting fiber from a solution of conducting polymer by the wet-spinning method. For example, polyaniline (PAn) conducting fibers having a conductivity of 10^2 S/cm were obtained by continuous dry-jet wet spinning of a solution of PAn in 1,4-diaminocyclohexane in a coagulation bath containing water or a water-dimethylformamide mixture.⁴ The properties of the conducting fibers prepared by this method significantly depended on the type of solvent used in the coagulation bath.⁵

Another approach for preparing conducting fibers is to use solutions containing both conducting and

nonconducting polymers together. In this way, fibers in which the conductivity changed with the PAN content were obtained by wet spinning from a concentrated sulfuric acid solution containing both PAn and poly(ω -aminoundecanoyle).⁶ It was also reported that fibers having a conductivity of 10^{-3} S/cm were prepared by the wet-spinning method from a solution of dodecylbenzenesulfonic acid doped PAn and polyacrylonitrile (PAN) polymer.⁷ The thermal stability of these composite fibers was better than those of their components.

The polymerization of aniline in the presence of sulfonated polystyrene by horseradish peroxidase enzyme has given a water-soluble PAn, and the fibers obtained by a dry-spinning technique from a solution containing both PAn and sulfonated polystyrene in water have shown a certain degree of orientation and crystallization.⁸

The *in situ* polymerization of a monomer to give a conducting polymer with a suitable oxidant in the presence of natural or synthetic fibers has also been used for the preparation of conducting fibers. The composite fibers prepared by this method with the polymerization of pyrrole onto fibers such as cotton, viscose, cupro, and Lyocell showed a certain degree of conductivity, depending on the polypyrrole (PPy) content of the fibers.⁹ In another study, it was stated that the resistivity of wool coated with PPy improved, and the composite fibers were suitable for dry-cleaning treatments.¹⁰ Dong et al.¹¹ found that

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the PAN coating thickness was around 30 nm in coaxial fibers obtained by the coating of PAN onto poly(methyl methacrylate) fibers prepared with electrospinning. It was reported that the composite fibers of nanocellulose and PPy prepared by *in situ* chemical polymerization had a surface area of 90 m²/g and a conductivity of 1.5 S/cm.¹² Beneventi et al.¹³ coated PPy onto the surface of cellulose fibers using an FeCl₃ impregnation–pyrrole polymerization sequence. Another method used to prepare conducting fiber is the adsorption of polyelectrolytes onto fibers. This method has mostly been applied by various workers to cellulose fibers.^{14,15} It was observed that the conductivity of poly(3-octylthiophene) nanoparticle adsorbed cellulose fibers reached 6×10^{-4} S/cm after iodine doping.¹⁶ Vapor-phase polymerization can also be used to obtain conducting fiber composites. Dall'Acqua et al.¹⁷ reported PPy dispersed at nanoparticle size in a cellulose matrix prepared by pyrrole vapor polymerization onto cellulose textiles.

In this work, we report for the first time the preparation of PPy/PAN composite fibers by the *in situ* chemical polymerization of pyrrole in the presence of PAN fibers with potassium persulfate as the oxidant. The effects of the time, temperature, and concentrations of oxidant, acid, and pyrrole on the surface resistivity and PPy content of the composite fibers were investigated in detail. The composite's possible use as a humidity and temperature sensor was investigated by the monitoring of its resistivity against the humidity and temperature of the medium. Mechanical tests, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis, and scanning electron microscopy (SEM) techniques were used for the characterization of the prepared composite fibers.

EXPERIMENTAL

Materials

The PAN fibers (580 denier) used in this study were supplied by AKSA Co. (Bursa, Turkey). Pyrrole obtained from Sigma-Aldrich (St. Louis, US) was used freshly after vacuum distillation. Potassium persulfate, acids, and solvents obtained from Merck (Schuchardt, Germany) were used without further purification.

Preparation of the conducting PPy/PAN composite fibers and PPy

PAN fibers prepared as 0.30 ± 0.01 g hanks were used in the experiments. Polymerization was carried out in a glass tube (10 cm in length, 4 cm in diameter) equipped with a magnetic bar. Fiber samples were put in an acidic aqueous solution of pyrrole at a certain concentration, and the polymerization was

started by the dropwise addition of potassium persulfate solution prepared in the same acid solution to the mixture. At the end of the polymerization, which was carried out at a definite temperature and for a previously determined period, the composite fibers taken from the mixture were washed with water and then methanol and aqueous acid solution. The purified composite fibers were dried to a constant weight *in vacuo* at 50°C.

The percentage of PPy in the composite fibers was calculated with the weights of the PAN fibers before and after the polymerization process.

Pure conducting PPy was synthesized by the oxidative chemical polymerization of pyrrole (0.12M) with a potassium persulfate (0.03M) oxidant in an aqueous HCl (1.2M) medium for 2 h at 0°C. The polymer, obtained in powder form, was pelleted to measure the electrical resistivity.

Characterization

The surface resistivity of the PAN/PPy composite was measured by a two-probe technique with a Keithley 6517A electrometer at room temperature (Cleveland, US). The surface resistivity of each sample was calculated from the resistance value and the probe dimensions by eq. (1). The two probes were placed on the sample with a 1-cm distance between them, and the resistance read on the digital electrometer was recorded.¹⁸ The probes were cylindrical with a diameter of 0.5 mm and a surface area of 7.9×10^{-7} m². The load applied to the probes during the measurements was 0.3 kgf.

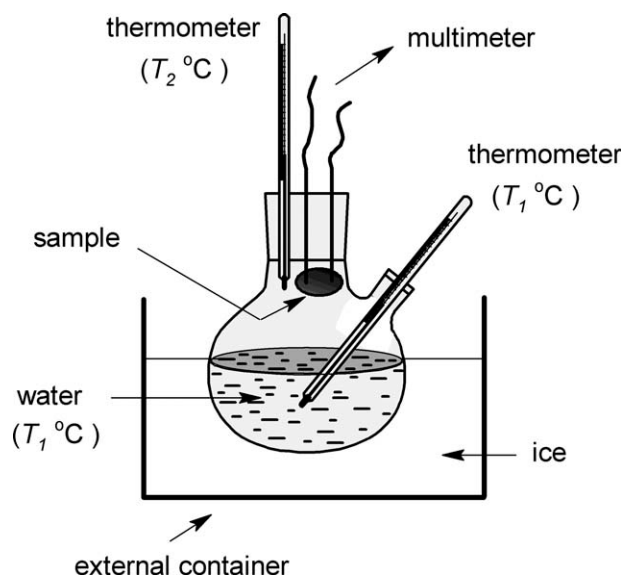
The average of 10 resistance measurements taken from different regions of the sample was used:

$$R = R_s \left(\frac{l}{w} \right) \quad (1)$$

where R is the resistance (Ω), w is the width of each electrode, and l is the distance between electrodes. R_s is sheet resistance of sample. The l/w ratio was 0.9 for the probe in the measurements.

The tensile strength and breaking elongation values were measured with a Hounsfield (Leeds, UK) tensile tester at 25°C. The jaw gap was 20 cm, and the extension rate was kept constant at 10 cm/min.

The FTIR spectra of the samples prepared as KBr pellets were obtained with a Mattson 1000 model FTIR spectrometer (ATI Unicam, UK). The thermal stabilities of the samples were investigated with a Shimadzu DTA-60H DSC-60 (Kyoto, Japan) thermal analyzer under an N₂ atmosphere between 25 and 650°C at a heating rate of 10°C/min. The surface morphologies of the pure PAN fiber and PAN/PPy composite fibers were examined with a JEOL model JSM 6060 LV (Tokyo, Japan) scanning electron



Scheme 1 Schematic of the RH measurement system with two temperature methods.

microscope. A cross-sectional image was taken by a Leica model DM 4000B (Wetzlar, Germany).

Composite fibers prepared under the optimal conditions were immediately used in characterizations and sensing procedures.

Thermal-sensing properties

The composite fiber was attached between two copper wires by a conducting adhesive and then placed in a glass cell. The cell was put into a bath at 5°C. The surface resistivity of sample was continuously recorded starting from 5°C up to 120°C at a heating rate of 2°C/min and was monitored again during cooling to 5°C from 120°C. These heating-cooling cycles were repeated five times.

Humidity-sensing properties

The relation between the humidity and resistivity of the composite was determined with a method that was previously explained in detail.^{19,20} Changing and measuring the humidity were carried out by a two-temperature method in a dynamic humidity chamber consisting of a 500-mL flask with two necks; one for the thermometer and the other for the fiber sample attached between the two copper wires. After some water was added to the flask, it was placed in an external container and filled with ice up to the level of water in the flask (Scheme 1). The temperature of this system was adjusted by the addition of necessary amounts of water and ice into the external container, and in this way, the temperature of the water (T_1) in the flask was kept at the required value. Thus, different humidity values

were obtained in the system. The temperature of the sample (T_2) was read from the thermometer placed in the position closest to it and attached at height of 6 cm from surface of the water in the flask. The humidity inside the chamber was calculated with the ratio of the saturated water vapor pressure at T_1 to that at T_2 . The values of the saturated vapor pressure were obtained from the *Chemical Engineers' Handbook*²¹

The relative humidity values in the air of the flask were calculated from the following equation:

$$\text{Relative humidity (\%)} = \frac{E_w(T_1)}{E_w(T_2)} \times 100 \quad (2)$$

where $E_w(T_1)$ is the saturated water vapor pressure at the water temperature and $E_w(T_2)$ is the saturated water vapor pressure at the sample temperature.

RESULTS AND DISCUSSION

Effect of the acid type

The effects of the type of acid on the PPy content and surface resistivity of the PAN/PPy composite fibers were investigated by the testing of seven different acids, and the results obtained are given in Table I. The polymerization reactions were carried out at 20°C for 2 h at an acid concentration that was 10 times the pyrrole concentration.

There have been some reports showing that the acid type used in the synthesis of conducting polymers does not have any strong effects on the yield and conductivity of polymer.²² However, there is also some data in the literature showing that the yield and conductivity of conducting polymers are closely related to the bulk volumes of dopants used.²³ Our experimental results showed that aqueous HCl was the most suitable medium among the acids tested for obtaining composite fibers having high PPy contents and low surface resistivities (Table I). So, HCl was selected for later experiments as

TABLE I
Effect of Acid Type on the PPy Content and Surface Resistivity of the PPy/PAN Composite Fibers

Acid type	pH	PPy (%)	Surface resistivity (k Ω /cm ²)
Hydrochloric acid	0.49	1.48	2.5
Perchloric acid	0.92	0.67	16.7
Nitric acid	0.65	0.53	19.5
Sulfuric acid	0.67	0.63	106.5
Phosphoric acid	1.27	0.42	187.5
Acetic acid	2.45	0.15	878.3
Formic acid	2.04	0.29	1032

[Pyrrole] = 0.06M, [Acid] = 0.6M, [Potassium persulfate] = 0.03M, temperature = 20°C, and time = 2 h.

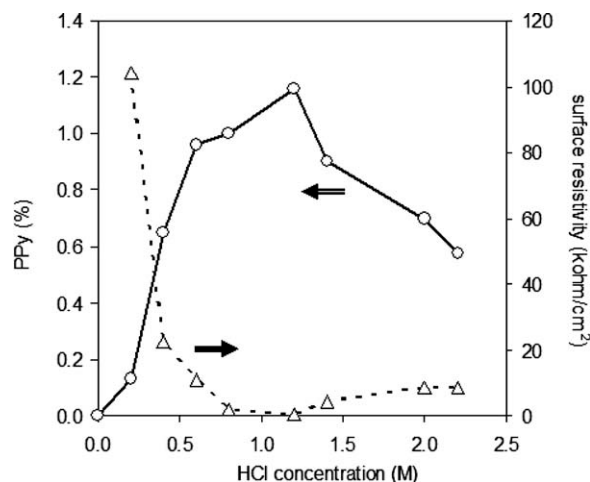


Figure 1 Effect of the HCl concentration on the (○) PPy content and (△) surface resistivity of the PPy/PAN composite fibers. ([Pyrrole] = 0.06M, [Oxidant] = 0.03M, polymerization temperature = 0°C, and time = 2 h.).

the polymerization medium. The mechanical properties of the fibers obtained in the HCl medium were also satisfactory for handling. On the other hand, the composite fibers prepared in perchloric acid medium showed brittle behavior after the drying process, and the fibers prepared in nitric acid medium, which were dark green–black in color, turned brown after the drying process.

Effect of the HCl concentration

The effects of the HCl concentration on the PPy content and surface resistivity of the PPy/PAN composite fibers were investigated in a separate experiment set (Fig. 1).

The composite fibers having the highest PPy content of 1.14% were obtained in 1.2M HCl medium, and PPy content was observed to decrease at higher acid concentrations. The HCl concentration of 1.2M was also observed to be favorable for preparing the composite fibers because of low surface resistivity. As shown in Figure 1, the surface resistivity of the fibers decreased up to this acid concentration and then climbed slightly. The measured pH values of the HCl concentrations used in the study were between 0.27 and 0.92.

The observation of an optimal acid concentration for the highest PPy content and the lowest surface resistivity could be explained by the oxidizing behavior of potassium persulfate in the medium having a different pH. At low pH values, it is known that the decomposition of potassium persulfate increases the concentration of H_2SO_5 .²⁴ The excess formation of H_2SO_5 in the polymerization medium caused the hydrolyzation of PPy polymer chains and decreased the PPy content of the com-

posite. The cutting of PPy polymer chains on the surface due to hydrolysis decreased the conductivity of the composite.

Effect of the polymerization temperature and time

Figure 2 shows the changes in the PPy content and surface resistivity of the composite fibers with polymerization temperature and time. The experiments carried out at temperatures between 0 and 60°C showed that the PPy contents of the composites increased with increasing temperature, and a composite fiber having the highest PPy content of 1.82% was obtained at 60°C for a polymerization of 2 h. It was also observed that 2 h was approximately the optimum polymerization time for obtaining composite fibers having the highest PPy content for all of the other temperatures examined. At prolonged polymerization times, both the PPy content and conductivity of the composites exhibited a slight decreasing tendency due to the overoxidation of PPy because the contact time with the oxidative solution was longer.²⁵

It can be seen in Figure 2 that the composite fibers having the lowest surface resistivity were obtained at 0°C. Although the surface resistivities of the composite fibers obtained at 20 and 40°C were relatively high, they were close to the data obtained at 0°C. However, the surface resistivity of the composite fibers obtained at 60°C was significantly higher than those of the fibers obtained at other temperatures.

At higher temperatures, polymerization occurs more readily and quickly; this results in a greater amount of insoluble polymers in solution.²⁶ Thus, weak chain conjugation leads to an increase in the

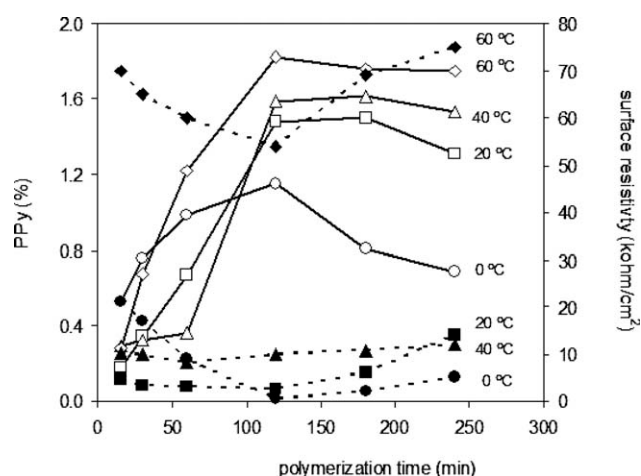


Figure 2 Effect of the polymerization temperature and time on the PPy content [(○) 0, (□) 20, (△) 40, and (◇) 60°C] and surface resistivity [(●) 0, (■) 20, (▲) 40, and (◆) 60°C] of the PPy/PAN composite fibers ([Pyrrole] = 0.06M, [Oxidant] = 0.03M, [HCl] = 1.2M).

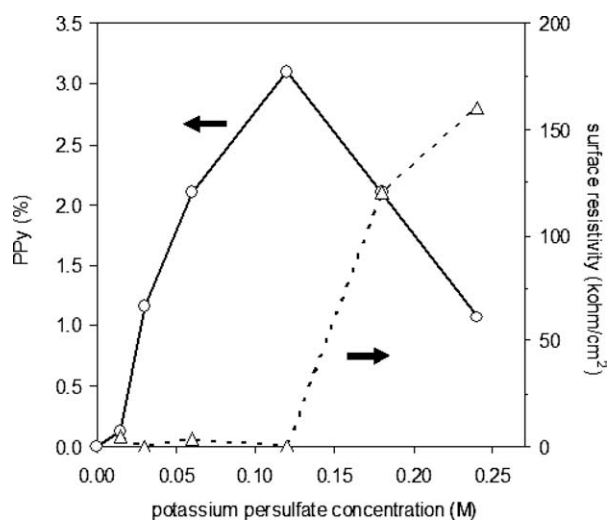


Figure 3 Effect of the potassium persulfate concentration on the (○) PPy content and (△) surface resistivity of the PPy/PAN composite fibers ([Pyrrole] = 0.06M, [HCl] = 1.2M, polymerization temperature = 0°C, and time = 2 h).

surface resistivity of a polymer (i.e., a decrease in conductivity). Considering the lowest surface resistivity, we decided to carry out the later experiments at 0°C.

Effect of the oxidant concentration

The effects of the potassium persulfate concentration on the PPy content and surface resistivity of PPy/PAN composite fibers are shown in Figure 3. The PPy content of the composite fibers increased with increasing potassium persulfate concentration in the range 0.015–0.24M, and its highest value of 3.1% was obtained at 0.12M. However, the PPy content was found to decrease beyond this potassium persulfate concentration.

At higher oxidant concentrations, the number of monomeric active centers formed in the polymerization medium increased. Because monomer molecules would be shared by these excess centers, the rate of dispersion polymerization, which led to the formation of dispersed PPy particles, increased. On the other hand, the PPy content of the composite decreased because of the slow surface polymerization rate, which led to PPy coating of the PAN fibers.

The composite fibers having the lowest surface resistivity were obtained at a potassium persulfate concentration of 0.03M. The increase in the surface resistivity observed at higher oxidant concentrations was due to the interaction of more persulfate ions with PPy chains. Excessive persulfate ions, which increased the oxygen content of the PPy chain, led to the formation of carbonyl groups on the chains via excessive oxidation of the polymer chains. Thus,

the surface resistivity of the composite fibers increased because of interruptions in the chain conjugations due to the carbonyl groups formed.²⁰

Effect of the pyrrole concentration

With an increase in the pyrrole concentration up to 0.12M, the PPy content of the composite fibers rapidly increased up to a value of 1.14% (Fig. 4). However, beyond a pyrrole concentration of 0.12M, the rate of increase of the PPy content decreased significantly. At higher pyrrole concentrations, the polymerization became effective in solution, and the PPy coating previously formed on the PAN restricted the diffusion of reactants to the surface of the fibers.

The lowest surface resistivity (0.6 kΩ/cm²) of the composite fibers was reached at pyrrole concentration of 0.06M, and the surface resistivity did not significantly change with increasing pyrrole concentration. Because relatively short chains would be formed at low monomer concentrations, the surface resistivity of the composite was high.²² When the pyrrole concentration was higher than 0.06M, the surface resistivity of the fibers decreased as a result of increasing chain conjugation due to the extended chain length. Over a certain chain length, as observed for the other physical properties of conducting polymers, such as the density and viscosity, the surface resistivity also did not change significantly.

Tensile strength and breaking elongation

The changes with PPy content of the mechanical properties, such as tensile strength and breaking elongation, of the PPy/PAN composite fibers were examined in five different composite fiber samples

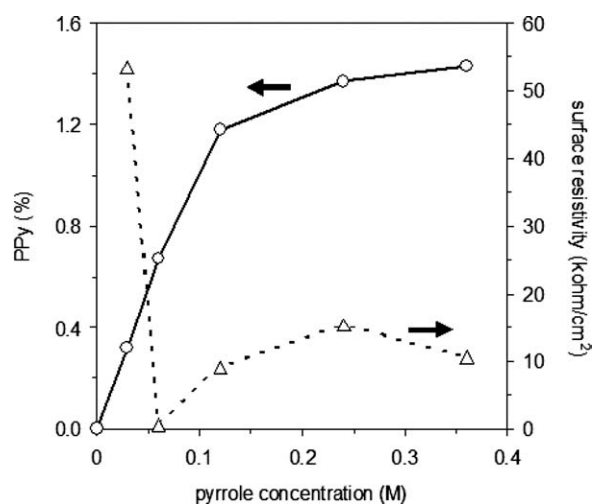


Figure 4 Effect of the pyrrole concentration on the (○) PPy content and (△) surface resistivity of the PPy/PAN composite fibers ([Oxidant] = 0.03M, [HCl] = 1.2M, polymerization temperature = 0°C, and time = 2 h).

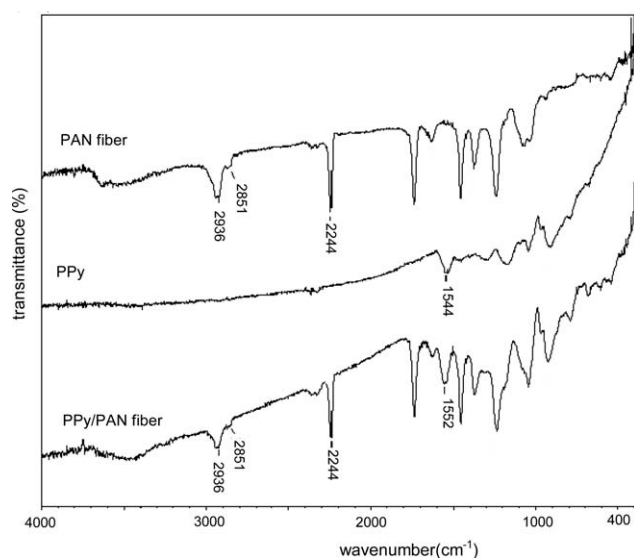


Figure 5 FTIR spectra of the (a) pure PAN fiber, (b) HCl-doped PPy, and (c) PPy/PAN composite fiber containing 1.14% PPy.

having the same PPy content. The standard deviations were calculated and found to be 0.8 and 1.7 for the force and elongation, respectively.

The PPy content of 0.13% seemed to be a critical value for both mechanical properties. Tensile strength (average = 10.5 N/m²) and breaking elongation (average = 29.2%) of the composite fibers improved up to this value because of the strong interaction forces between the PPy and PAN in the composite compared with those of the individual components. With a PPy content of greater than 0.13%, the tensile strength and breaking elongation exhibited decreases (8.8 N/m² and 28.2%, respectively) because of the weak mechanical properties of PPy.^{27,28}

Environmental stability

The surface resistivity of the PPy/PAN composite fibers containing 1.14% PPy was periodically measured under atmospheric conditions for 78 days. It was observed that the surface resistivities of the composite fibers increased up to the 17th day and then became stable. This phenomenon could be interpreted with the decrease of charge carriers on the chain due to the interaction of O₂ in the air with carbenium ions at the polymer chains, which resulted in an increase in the surface resistivity with time.²⁵ Additionally, the escape of dopant Cl⁻ anions from the composite could have played a role in the increase in surface resistivity.

FTIR spectra

To illustrate the structural changes before and after polymerization, the FTIR spectra of the original

PAN fibers, pure PPy, and PAN/PPy composite fibers containing 1.14% PPy were recorded in the range 4000–400 cm⁻¹. As shown in Figure 5, the spectrum of the composite had a characteristic pyrrole ring peak at 1552 cm⁻¹, originating from PPy, peaks of –C≡N stretching at 2244 cm⁻¹, and symmetrical and antisymmetrical C–H stretching at 2851 and 2936 cm⁻¹, respectively, coming from PAN, which was the other component of the composite [Fig. 5(c)]. The shifting of the pyrrole ring peak from 1544 to 1552 cm⁻¹ in the spectrum of the composite fiber [Fig. 5(b)] indicated that H bonds were formed between the fiber and PPy chains.

Thermogravimetric analysis

The thermogram of the PPy/PAN composite fiber [Fig. 6(c)] was similar to that of pure PAN fiber [Fig. 6(a)], which was the dominating component of the composite, with some differences. For example, the main weight loss observed for the pure PAN at 300°C shifted to 286°C for the composite fiber because of its PPy content. On the other hand, pure PAN lost 73% of its total weight at 600°C; the composite fiber lost only 59%. The total weight loss of PPy, which was the other component of the composite, at this temperature was around 51%. These observations indicated that the thermal stability of the PPy/PAN composite fiber was between the thermal stabilities of its components of PAN and PPy and was higher than that of pure PAN.

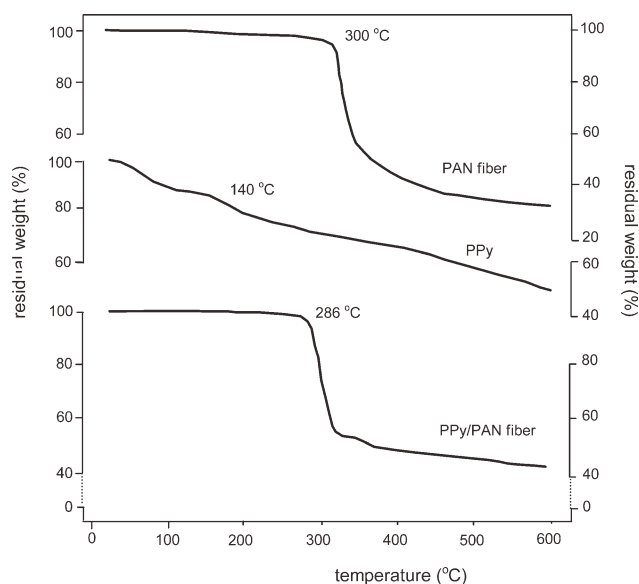


Figure 6 Thermograms of the pure PAN fiber, HCl-doped PPy, and PPy/PAN composite fiber containing 1.14% PPy. The composite fiber sample was obtained under the following conditions: [Oxidant] = 0.03M, [Pyrrole] = 0.06M, [HCl] = 1.2M, polymerization temperature = 0°C, and time = 2 h.

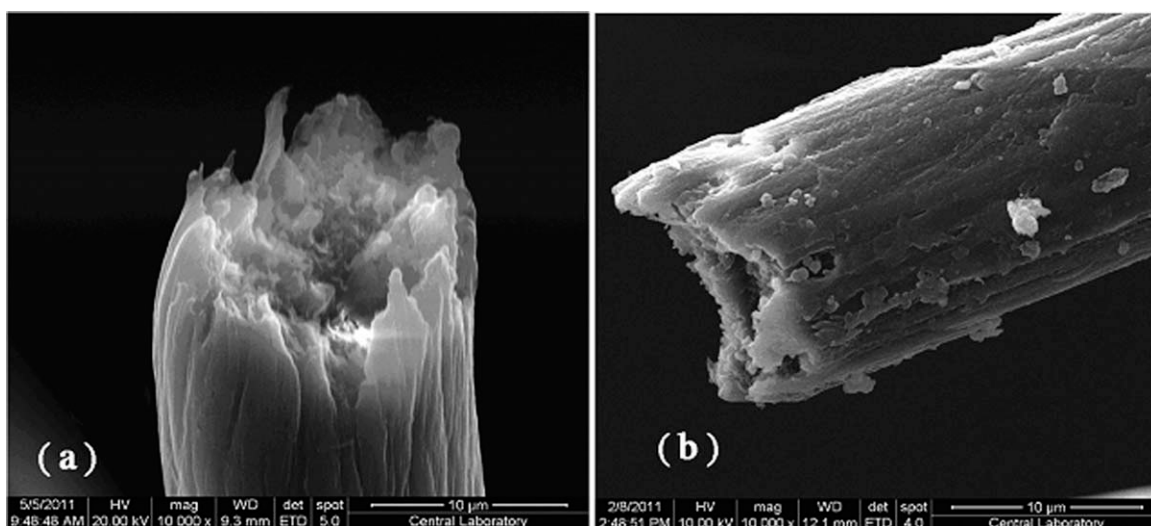


Figure 7 SEM micrographs of the (a) pure fractured PAN fiber and (b) fractured PPy/PAN composite fiber containing 1.14% PPy.

The one-step degradations starting at 300°C [Fig. 6(a)] and 286°C [Fig. 6(c)] corresponded to the decomposition temperatures of the pure and composite PANs, respectively.

SEM and cross-sectional images

Figure 7 shows the micrographs of the pure PAN and PPy/PAN composite fiber containing 1.14% PPy. Clearly noticeable lines in the form of slits parallel to the longitudinal axis of fiber and relatively deep at some regions were observed in the micrograph of the pure fiber [Fig. 7(a)]. Such lines were also noticeable on the surface of the composite fiber [Fig. 7(b)], but they were not so clear as in the pure PAN because of the PPy coating. We concluded from the SEM image of the composite that PPy was physically coated onto the surface of the fibers. Furthermore, there were particles and agglomerations of PPy at some regions on the composite fiber surface in various sizes. Additionally, there was not any deformation along the longitudinal axis of the fiber.

Cross-sectional images of the composite fiber supported this observation. We obtained cross-sectional images of the composite fibers, given in Figure 8, and these images were very similar to that of the pure PAN.²⁹

Indeed, the cross-sectional images of the composite were circular and are indicated with an arrow in Figure 8. However, during the preparation of the samples with a microtome for optical microscopy, the cross-sectional geometries of most of the fibers were deformed and had a shape like a bean, as shown in the figure.

Humidity-sensing properties

The humidity-sensing properties of the pure PPy and PPy/PAN composite fiber containing 1.14% PPy

were examined separately by measurement of the surface resistivities with changing relative humidity of the environment [Fig. 9(a,b)].

As shown in Figure 9(a), an increase in the relative humidity caused a decrease in the surface resistivity of the pure PPy. The reason for this phenomenon was mainly ascribed to the proton exchange between the adsorbed water molecules and the composite. At high humidity, a continuous layer of water molecules on the surface of the composite fiber formed. In this continuous layer, the transfer of H^+ or H_3O^+ became fast, and the resistivity of the composite decreased.^{30,31}

Contrary to that in pure PPy, the surface resistivity of the composite fibers increased as the humidity increased [Fig. 9(b)]. One of the reasons for this observation was that the H bonds between NH groups

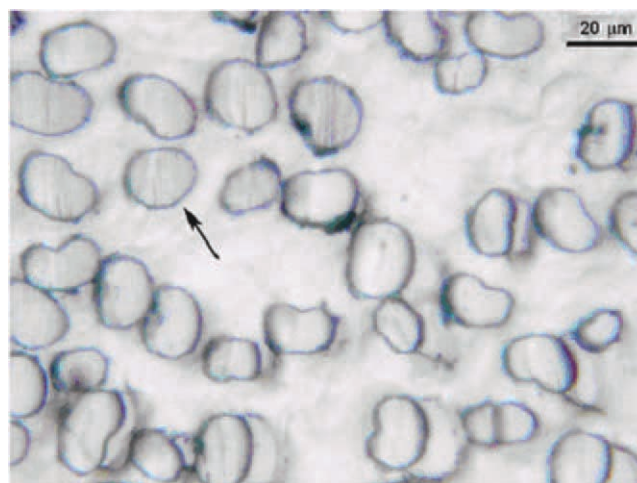


Figure 8 Cross-sectional images of the PPy/PAN composite fiber containing 1.14% PPy recorded with optical microscopy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

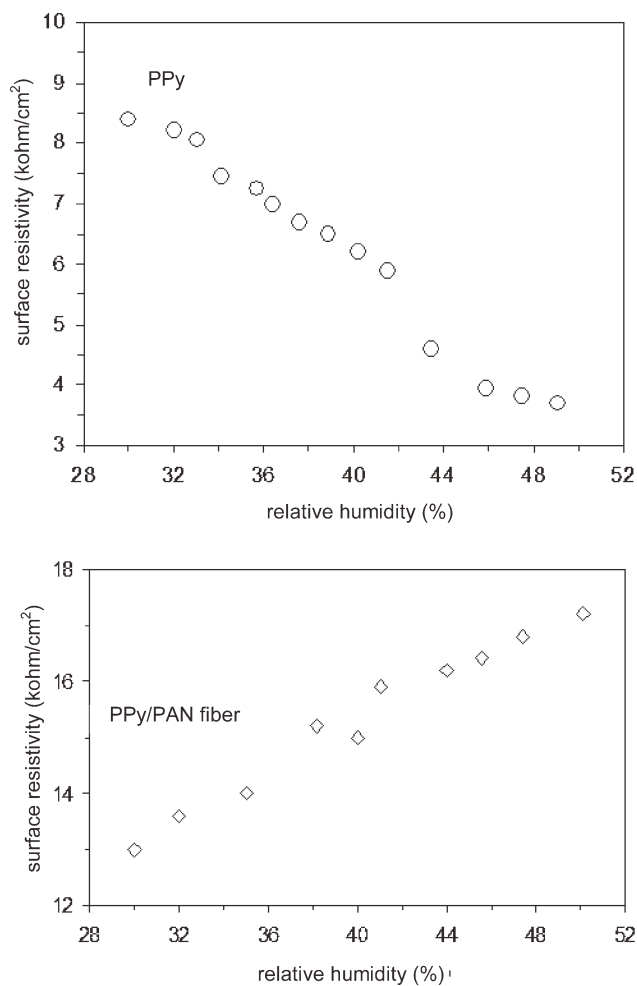


Figure 9 Change in the surface resistivity of the (○) pure PPy and (◇) PPy/PAN composite fiber with the relative humidity.

on the PPy and $-\text{C}\equiv\text{N}$ on the fiber decreased the interaction of water molecules with PPy chains. In this case, with increasing humidity, free water molecules prevented the mobility of ions interacting with Cl^- dopant and increased the conductivity. Another reason was the plasticizer effect of water on the PAN fiber, which had a polar structure. Because of this effect, the PPy coating on the surface of the fiber loosened, and therefore, the percolation process between PPy particles weakened, and this resulted in an increase in the surface resistivity [Fig. 9(b)].

Temperature-sensing properties

The temperature-sensing properties of the PPy/PAN composite fiber and pure PPy were examined by the monitoring of the surface resistivity values during heating–cooling cycles five times between 5 and 120°C (Fig. 10).

The surface resistivity of the pure PPy decreased during heating from 5 to 120°C, except in the 80–

120°C range of the first cycle [Fig. 10(a)]. However, an increase in the surface resistivity of pure PPy was observed during the cooling cycle in the same temperature range. However, as can be seen from the figure, the resistivity values recorded during the heating and cooling cycles were not orderly, and there were fluctuations as increases and decreases. Furthermore, the resistivity values of pure PPy measured at each cycle between 5 and 120°C were not reproducible.

The relationship of the resistivity and temperature for the PPy/PAN composite fiber in the same temperature range was more orderly and repeatable [Fig. 10(b)] compared to that for pure PPy. Especially after the first two cycles, the composite fiber became more stable, and reproducible surface resistivity values were obtained in the next cycles. These results indicate that the PPy/PAN composite fiber is a material with potential use as a thermal sensor within this temperature range.

The temperature–resistivity correlation of the PPy/PAN composite fiber was similar to the behavior of conducting polymers in general, and the surface resistivity of the composite fiber decreased with increasing temperature, as also observed for PPy. One of the effects of the decreasing surface resistivity was the increase in the charge-transfer effectiveness between polymer chains and dopants with increasing temperature.³²

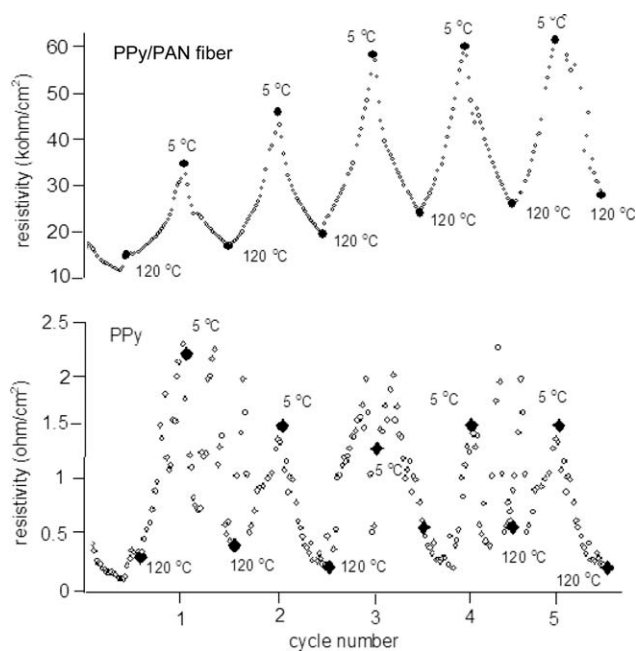


Figure 10 Change in the surface resistivity of the pure PPy and PPy/PAN composite fiber containing 1.14% PPy during heating–cooling cycles with five repetitions in the temperature range from 5 to 120°C.

CONCLUSIONS

The results obtained in this study indicate that a conducting PPy/PAN composite fiber could be prepared by the polymerization of pyrrole in the presence of PAN fiber with potassium persulfate as the oxidant. Composite fibers with PPy contents within the range 0.08–3.1% and surface resistivities within the range 175–0.6 kohm/cm² were prepared through changing polymerization conditions. It was observed that a PPy content of 0.13% was the optimal value for obtaining composites fiber having the highest tensile strength. The cross-sectional images of the composite showed that the PPy coating was restricted to only the surface of the fiber and did not penetrate toward the fiber center. The surface resistivities of the composite fiber reached a stable value after 17 days under atmospheric conditions. The temperature–surface resistivity correlation of the composite fiber was more orderly and reproduceable compared to that of pure PPy. Another result obtained in this study was that, whereas the resistivity of the homopolypyrrole decreased with increasing humidity, the resistivity of the composite increased.

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