Preparation and Properties of Polyaniline Electrospun Fiber Web

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ABSTRACT: The objective of this study is to fabricate the highly electrical conducting polymer fibers applicable to many conducting materials. Therefore, we tried to prepare polyaniline (PANI) thin fiber web by an electrospinning process by the following steps. First, PANI emeraldine base (EB) was prepared by oxidative polymerization. Second, the PANI EB was doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), and subsequently that was dissolved in trifluoroacetic acid (TFA). Third, the PANI-AMPSA solution was electrospun by an electrospinning process. Consequently, the PANI doped with AMPSA was successfully electrospun into thin fiber form, and the electrical conductivity was superior. Also, the electrical conductivity of the PANI-AMPSA electrospun was increased by a simple redoping process with AMPSA. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4033–4037, 2012

Key words: electrospinning; conducting polymer; polyaniline (PANI); nanofiber; doping

INTRODUCTION

With the discovery in 1960 of intrinsically conducting polymers (ICPs), an attractive subject of research was initiated because of the interesting properties and numerous application possibilities of ICPs. It was expected that ICPs would find their potential applications in multidisciplinary areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane, and sensors.[1–4] However, many of the potential uses for ICPs have yet to be explored because of a number of obstacles that need to be overcome.[5] Among the ICPs, polyaniline (PANI) is regarded as one of the most technically promising conducting polymer because the monomer (aniline) is inexpensive, the polymer can be easily prepared by the simple oxidative polymerization with high yield, and products are stable under ambient condition.[6,7] However, the applications of ICPs including PANI are hampered by the poor mechanical properties, the lower level of conductivity compared with metal, and the infusibility and poor solubility in all available solvents.

Hence, much work has been done to develop different matrixes modified with PANI and to improve the solubility of PANI through doping with a suitable dopant or modifying the starting monomer.[5,8–10]

On the other hand, the electrospinning is a simple fiber-spinning technique that produces polymer fibers with nanometer-to-micrometer size diameter. Although the variation in the fiber diameter is large, the fibers prepared by this method typically have diameters much smaller than those attained using standard mechanical fiber-spinning technologies.[11] Hence, if PANI was introduced into electrospun fibers, electrically conducting nanowires could be fabricated.[7]

Therefore, we tried to prepare PANI electrospun thin fibers by the electrospinning process to use the PANI electrospun thin fibers in various applications. To electrospin PANI solution, PANI emeraldine base (EB) was dopped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and dissolved in various organic solvents. And, we optimized the electrospinning conditions to form the PANI electrospun thin fibers well.
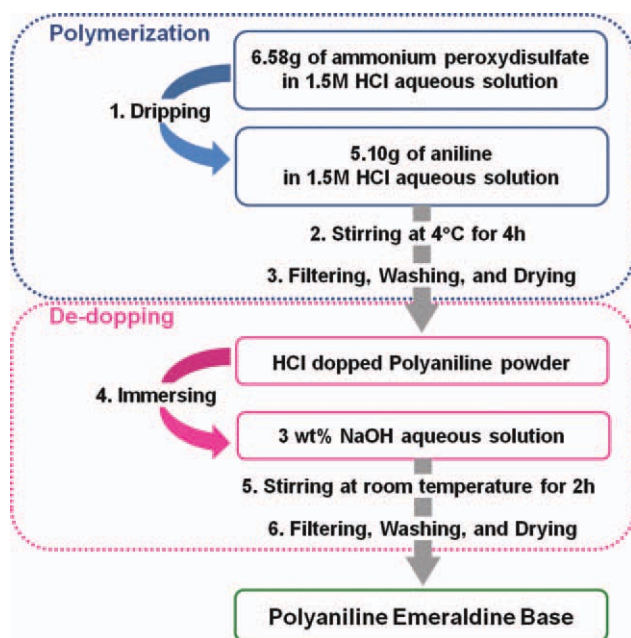
EXPERIMENTAL

Materials

Aniline (Ducksan Pure Chemical Co., Ansan, Korea) was distilled under vacuum before use. Cellulose acetate (CA) and AMPSA [$H_2C{=}CHCONHC(CH_3)_2$ CH_2SO_3Na] was purchased from Aldrich Co. (MO). The other chemicals including ammonium peroxydisulfate (APS)

Figure 1 Schematic diagram of PANI EB preparation process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

[$(NH_4)_2S_2O_8$], trifluoroacetic acid (TFA) [CF_3CO_2H], dichloroacetic acid (DCA) [$CHCl_2COOH$], N-methyl-pyrrolidone (NMP) [C_5H_9NO], m-cresol [C_7H_8O], sodium hydroxide [NaOH], formic acid [HCOOH], and hydrochloric acid [HCl] were purchased from Ducksan Pure Chemical Co. (Ansan, Korea) and used with reagent grade.

Preparation

Preparation of PANI EB

Distilled aniline (5.10 g) and APS (6.58 g) were separately dissolved in 1.5M HCl aqueous solution, respectively. And the aniline and APS solutions were mixed and reacted for 4 h at 4°C under stirring. After rinsing and drying, we obtained PANI emeraldine salt (ES) dopped by HCl with poor solubility in organic solvents. Then, PANI ES particles were immersed in 3% NaOH aqueous solution for 2 h under magnetic stirring. Subsequently, the dedopping solution was filtered and washed with distilled water, methanol, and acetone. The preparation procedure of PANI EB is briefly shown in Figure 1.

Preparation of spin dope

EB (1 g) was mixed with AMPSA (1.2 g) and ground together using a mortar and pestle in air for about 20 min. In a glass vial, 0.56 g of the powdered mixture was added to the following solvents: TFA, DCA, NMP, and m-cresol. And the solutions were stirred

by a magnetic stirrer until no particles were observed from the solution by an optical microscope. The acid chosen dopes the insulating EB to the conducting salt form of PANI and also has the solvating group necessary to dissolve it in the organic for postprocessing of the polymer in the conducting form.[12–14] CA/PANI-AMPSA electrospun fiber web was prepared for reference as follows: PANI-AMPSA was dissolved in HCOOH, and then, CA was added in the PANI-AMPSA solution. The ratio of PANI-AMPSA to CA was set for 2 : 4 and the concentration of the solution was set for 16.5% according to our previous study.

Electrospun fiber preparation

The electrospinning apparatus was shown in Figure 2. The hypodermic syringe used in these experiments had a capillary tip diameter of 20 gauge (diameter = 0.9 mm), and the tip was tilted about 10° relative to the vertical position. A positive potential was applied to the PANI/AMPSA solution by connecting a copper wire to the metal capillary, and the potential difference between the syringe and the counter electrode (collector) was 20~30 kV. A rotating drum covered with aluminum foil, placed 7 cm below the capillary tip, was used to collect the electrospun material.

Characterization

The morphology of the electrospun fibers was observed using field emission scanning electron microscopy (JOEL JSM-6340F; Japan) after applying a gold coating. The average diameter of the electrospun fibers was determined by analyzing the SEM images using a custom code image analysis program. Fourier
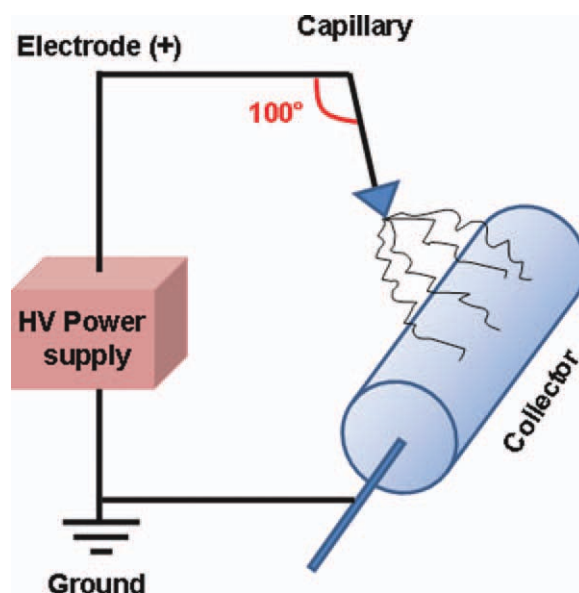
Figure 2 Schematic diagram of electrospinning apparatus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].
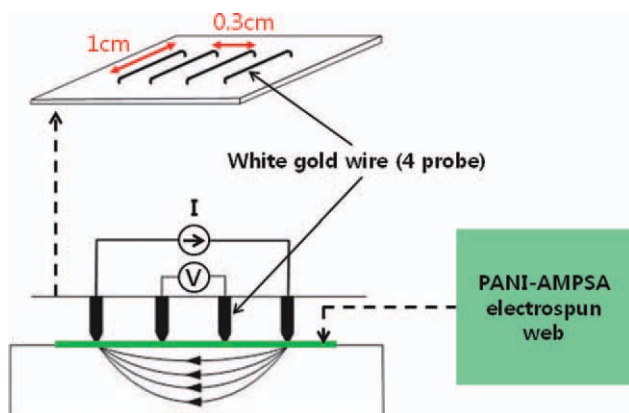
Figure 3 Schematic diagram of 4-probe line electrode. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

transform infrared (FTIR) spectroscopy was performed with a PerkinElmer Spectrum 2000 FTIR spectrometer with a resolution of 4 cm^{-1}, and the measurements were performed with a KBr support. X-ray diffraction (XRD) patterns of PANI-AMPSA electrospun webs were registered using a D8 Advance (Bruker, Germany) using Cu-Ka, 1.54187 Å radiation in as-prepared web state. The electrical conductivities of the electrospun fiber webs were measured by four straight lines probe (Fig. 3) connected to a Kithley 2400 digital source meter.[7,15] A constant current source was used to pass a steady current through the two outer probes in the surface of a specimen, and the voltage across the inner two was measured. The conductivity of a sample was determined with the following formula (1):

$$\sigma(\text{S/cm}) = l/dw \times I/V \qquad (1)$$

where, σ is the electric conductivity, l is the spacing between probes (0.3 cm), d is the thickness of the sample, W is the length of the line probe (1 cm), I is the current passed through the outer probes, and V is the voltage drop across the inner probes.
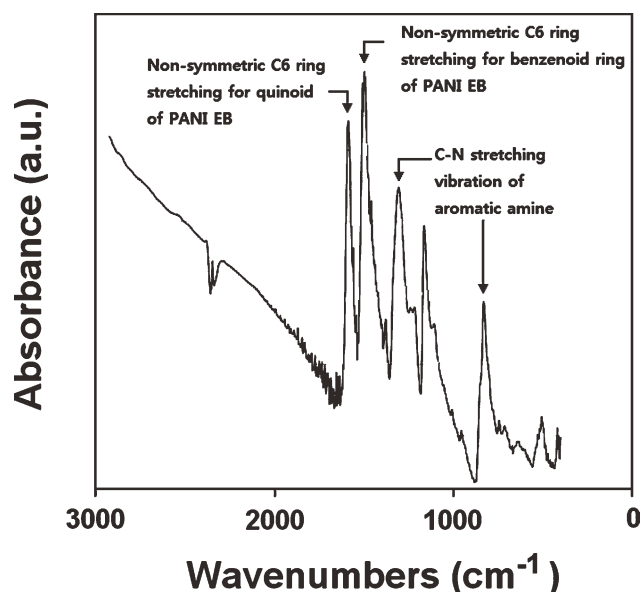
Figure 4 FTIR spectrum of PANI EB.

RESULTS AND DISCUSSION

Preparation and properties of PANI electrospun
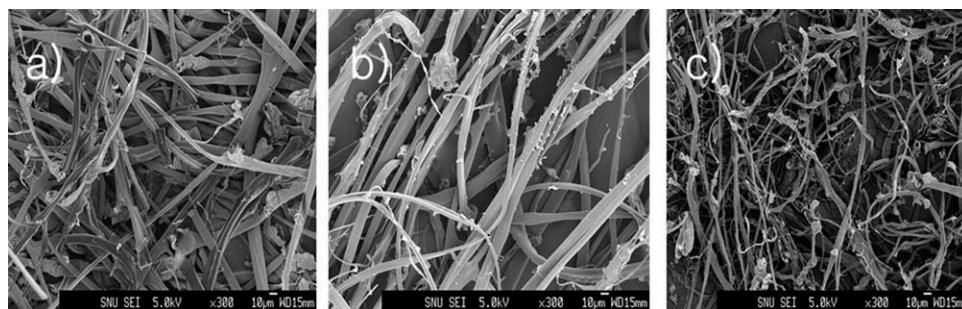
Preparation of PANI EB

Figure 4 shows the FTIR spectrum of PANI EB. Therefore, we confirmed that PANI EB was successfully prepared from the process Figure 1.[16]

Preparation of PANI dope

We tried to dissolve the as-prepared PANI EB and AMPSA mixed powder in several organic solvents, such as TFA, DCA, N-NMP, and m-cresol. And, we found that only TFA can dissolve the PANI-AMPSA mixture within a concentration of 10 wt %. In particular, it was observed that the PANI-AMPSA/TFA solution was electrospun into fiber form only in a concentration range from 8 to 10 wt % because the solution
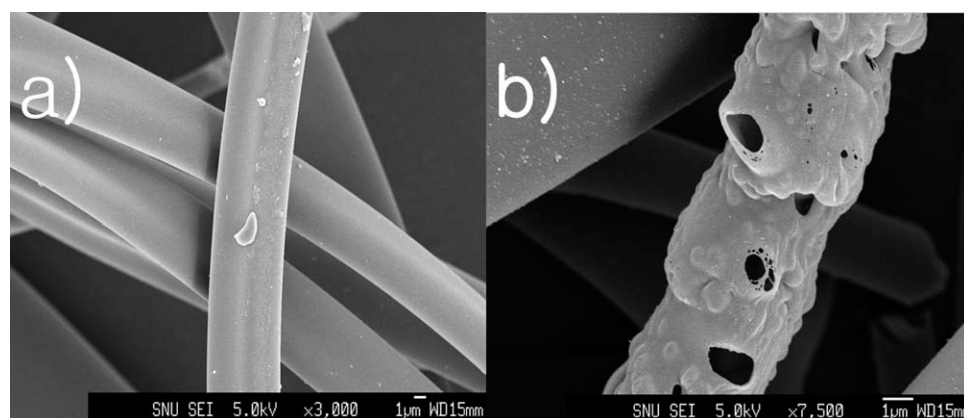
Figure 5 SEM micrographs of PANI-AMPSA electrospun fiber; solution concentration: 10 wt %, applied voltage: ca. 25 kV: (a) large-diameter fiber part and (b) small-diameter fiber part.

Figure 6 SEM micrographs of PANI-AMPSA electrospun fiber as a function of applied voltage; (a) 20 kV, (b) 25 kV, and (c) 30 kV.

below 8 wt % was so thin that it was sprayed into droplets through electrospinning process.

Preparation of PANI-AMPSA electrospun

Figure 5 shows the PANI-AMPSA electrospun fiber prepared from the 10 wt % solution at about 25 kV. As shown in the images, the fibers with large diameter [Fig. 5(a)] showed flat and ribbon cross-sectional shape, meanwhile the fibers with small diameter [Fig. 5(b)] showed porous structure. It appears that the fibers with large diameter have relatively small surface area compared with the fibers with small diameter. Therefore, the solvent evaporation rate of the large fibers must have been slow and the fibers might have met the collector before sufficiently solidified. However, in the case of the small fibers, the regular phase morphology seems to be generated by rapid phase separation during the electrospinning process. The solvent rich regions are apparently transformed into pores.[17] The vapor pressure of TFA (97.5 mmHg) is five times greater than that of water (17.54 mmHg). The effect of applied voltage on the formation of PANI-AMPSA electrospun fiber was investigated as shown in Figure 6 and Table I. It was observed that the fiber diameter decreased with increasing the applied voltage during electrospinning process. Even though there is a little dispute about the behavior of applied voltage in the electrospinning process, in general a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field, and these effects lead to reduction in the

fiber diameter and also rapid evaporation of solvent from the fibers results.[18] In addition, we observed the overall morphology of the fibers prepared at 30 kV (Fig. 5(c)) was relatively nonuniform from the images. This is presumed that the extremely high voltage applied at the end of PANI-AMPSA solution made the polymer jet instable during the electrospinning process. In general, when high voltage is applied during electrospinning, Taylor cone formation becomes stable and columbic repulsive force within the jet of spinning solution makes viscoelastic solution extended. If higher than critical voltage is applied, more charge will drop from the end of the needle due to the acceleration of charge, the Taylor cone becomes unstable.[18,19] In particular, Hayati et al.[20] have showed that highly conductive solutions are extremely unstable in the presence of strong electric fields, which results in a dramatic bending instability as well as a broad diameter distribution.

Properties of PANI-AMPSA electrospun

The crystallinity of PANI-AMPSA electrospun fiber web prepared at various electric voltages was investigated, as shown in Figure 7. Crystalline peaks of

TABLE I
Average Values and Standard Deviations of Fiber Diameters in PANI-AMPSA Electrospun Web as a Function of Applied Voltage

Applied voltage (kV)	Average diameter (μm)	Standard deviation
20	6.02	2.36
25	5.88	1.41
30	3.05	6.54
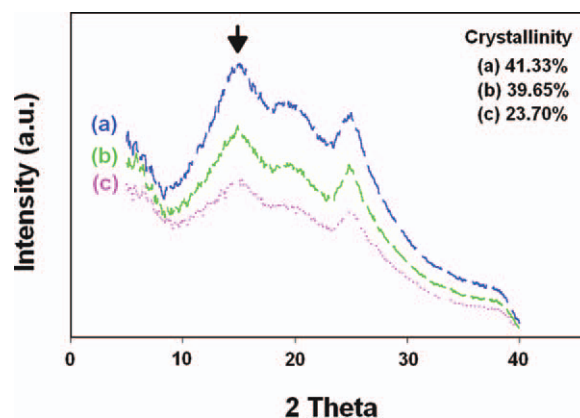
Figure 7 XRD patterns of ANI-AMPSA electrospun fiber as a function of applied voltage: (a) 35 kV, (b) 30 kV, and (c) 25 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

Applied voltage (kV)	20 kV	25 kV	30 kV	35 kV
PANI-AMPSA electrospun fiber web	1.225×10^{-4}	2.612×10^{-2}	8.876×10^{-2}	1.064×10^{-1}
CA/PANI-AMPSA electrospunn fiber web	1.225×10^{-8}	2.119×10^{-7}	1.756×10^{-6}	2.216×10^{-6}

PANI-AMPSA electrospun fiber web at around 15° were observed to increase with increasing the applied electric voltage, indicating that the crystallinity of PANI-AMPSA electrospun fiber increased as the electric power increased. It appears that the ejected polymer solution in the electrospinning process would be subject to high elongation at high electric voltages. Therefore, the polymer chains in the fibers are oriented to the fiber axis, and the crystallinity of the fibers increases. In addition, we found that the increased orientation and crystallinity of the fibers induced to raise the electrical conductivity of the PANI-AMPSA electrospun fiber web, as shown in Table II. This is because as the crystallinity of PANI increases, the charge carrier mobility of the conjugated polymer PANI increases due to the poor intergrain boundaries decrease between the microcrystalline domains.[21–23] On the other hand, we found that the electrical conductivity of the PANI-AMPSA electrospun fiber web was more increased from 8.875×10^{-2} to 1.304×10^{-1} by simple redopping process (immersing in a $1M$ of AMPSA solution for 2 h). And the level of electrical conductivity of the PANI-AMPSA electrospun fiber web was superior to that of other PANI-electrospun web prepared by PANI blending solution as shown in Table II.[24]

CONCLUSION

To fabricate highly electrical conducting fibers, we tried to electrospin conducting polymer PANI into the form of thin fibers web and investigated the properties by SEM, XRD, electrometer, etc. From the results, we found that the PANI doped with AMPSA was successfully electrospun into thin fiber form, and the electrical conductivity was superior to other PANI electrospun prepared by blending of conducting polymer and matrix polymer.[7,24] In particular, the PANI-AMPSA electrospun increased in the electrical conductivity by a simple redoping process. Therefore, we expected that the PANI-AMPSA electrospun fibers could be an applicable electrical materials and/or nanowires for connecting the microelectromechanical system in the future.

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