

Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends

Ian D. Norris^a, Manal M. Shaker^b, Frank K. Ko^b, Alan G. MacDiarmid^{a,*}

^a Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

^b Fibrous Materials Research Center, Department of Materials Engineering, Drexel University Philadelphia, PA 19104, USA

Received 7 December 1999; received in revised form 8 February 2000; accepted 10 February 2000

Abstract

Ultrafine fibers of polyaniline doped with camphorsulfonic acid (PAN.HCSA) blended with polyethylene oxide (PEO) were prepared by a non-mechanical, electrostatic spinning (“electrospinning”) technique. The morphology and fiber diameter of electrospun polyaniline blend fibers revealed that both the PEO and the PAN.HCSA/PEO blend fibers had a diameter ranging between 950 nm and 2.1 μm , with a generally uniform thickness along the fiber. The UV–visible spectra of these electrospun fibers were similar to those for cast films produced from the same solutions. As expected, the conductivity of the non-woven fiber mat, as measured by the four-point probe method, was slightly lower than that of a cast film, due to the high porosity of the non-woven mat. The rate for the vapor phase de-doping/re-doping of the electrospun fibers is at least one order of magnitude faster than for cast films, stressing the enormous effect an increase in the surface-to-volume ratio, accomplished by electrospinning the material into fibers, can have on the selected chemical properties of polyaniline blends. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrostatic fabrication; Ultrafine conducting fibers; Polyaniline/polyethylene oxide blends; Electrospinning

1. Introduction

Electrostatic generation of ultrafine fibers (“electrospinning”) has been known since the 1930s [1]. This technique has been recently rediscovered for applications such as high performance filters [2,3] and for scaffolds in tissue engineering [2,4] that utilize the unique characteristics of the high surface area ($\sim 10^3 \text{ m}^2/\text{g}$) provided by the fibers. In this non-mechanical, electrostatic technique, a high electric field is generated between a polymer fluid contained in a glass syringe with a capillary tip and a metallic collection screen. When the voltage reaches a critical value, the charge overcomes the surface tension of the deformed drop of the suspended polymer solution formed on the tip of the syringe, and a jet is produced. The electrically charged jet undergoes a series of electrically induced bending instabilities during its passage to the collection screen that results in the hyper-stretching of the jet. This stretching process is accompanied by the rapid evaporation of the solvent molecules that reduces the diameter of the jet, in a cone-shaped volume called the

“envelope cone”. The dry fibers are accumulated on the surface of the collection screen resulting in a non-woven mesh of nano to micron diameter fibers. The process can be adjusted to control the fiber diameter by varying the charge density and polymer solution concentration, while the duration of electrospinning controls the thickness of fiber deposition [5]. A schematic drawing of the electrospinning process is shown in Fig. 1.

Considering the well-known fact that the rate of electrochemical reactions is proportional to the surface area of the electrode, we are interested in exploiting the high surface to volume ratio of electrospun fibers to develop porous polyaniline electrodes. Reneker and Chun [5] have reported that polyaniline fibers can be successfully electrospun from sulfuric acid into a coagulation bath. Another way of producing electrically conductive nanofibers is, as reported by Chun et al. [6], by the pyrolysis of electrospun polyacrylonitrile nanofibers into carbon nanofibers. However, the conductivity value of neither the electrospun polyaniline nor the carbon nanofibers was reported.

In this paper, we describe a novel technique for the production of ultrafine electrically conducting fibers to form a non-woven mat using a polyaniline/polyethylene

* Corresponding author.

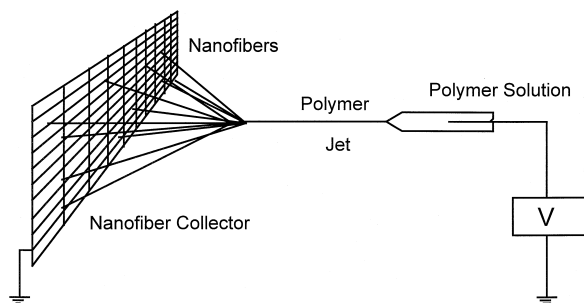


Fig. 1. Schematic of the electrospinning process.

oxide (PEO) blend dissolved in chloroform. A unique characteristic of these polyaniline blend fibers is their electroactive nature (i.e. their electronic, magnetic, optical and associated properties which respond to external influences).

2. Experimental

2.1. Materials

PEO (M_w 900,000 Da) and 10-camphorsulfonic acid (HCSA) and chloroform were purchased from Aldrich; the emeraldine base (M_w 120,000 Da) was supplied by Neste Oy. These chemicals were used without further purification.

2.2. Solution preparation

Various polymer blend solutions were prepared with the concentration of polyaniline doped with HCSA (PAn.HCSA) ranging from 0.5 to 2 wt.% and the concentration of PEO ranging from 2 to 4 wt.%. By varying the ratio of polyaniline to PEO, the concentration of doped polyaniline in the PEO matrix varied between 11 and 50 wt.%. These polymer blend solutions were prepared by first dissolving the exact amount of HCSA required to fully dope the emeraldine base in chloroform. The emeraldine base was slowly added to the chloroform solution with vigorous stirring at room temperature. This solution was allowed to stir for 2 h and subsequently filtered using a No. 42 Whatman filter paper to remove any particulate matter. The PEO was then slowly added to the doped polyaniline solution over a period of 1 h with magnetic stirring to obtain a homogeneous solution.

2.3. Electrospinning experiments

The electrospinning apparatus, as shown in Fig. 1, used a variable high voltage power supply purchased from Gamma High Voltage Research. The glass pipette used in these experiments had a capillary tip diameter of 1.2 mm, and the pipette was tilted at approximately 5° from hori-

zontal so that a small drop was maintained at the capillary tip due to the surface tension of the solution. Alternatively, to produce larger quantities of electrospun fibers, the glass pipette in the above set-up was replaced by a 5-ml glass syringe with a Becton Dickinson 18 hypodermic needle. The tip of the needle was filed to produce a flat tip. A positive potential was applied to the polymer blend solution, by inserting a copper wire into the glass pipette or by attaching the lead to the high voltage power supply directly to the outside of the hypodermic needle. The collection screen was a 10 × 10 cm copper plate placed 25 cm horizontally from the tip of the pipette as the grounded counter electrode. The potential difference between the pipette and the counter electrode used to electrospin the polymer solution was 25 kV (electrical field strength, 1 kV/cm).

2.4. Characterization of electrospun fibers

The fiber diameter and polymer morphology of the electrospun PAn.HCSA/PEO fibers were determined using scanning electron microscopy (SEM). A small section of the non-woven mat was placed on the SEM sample holder and sputter-coated with gold (Denton Desk-1 Sputter Coater). An Amray 3000 SEM using an accelerating voltage of 20 kV was employed to take the SEM photographs.

The conductivity of the electrospun PAn.HCSA/PEO fibers and the cast film on a microscope glass slide was measured using the four-point probe method [7]. The thickness of the non-woven fiber mat and the cast films were measured using a digital micrometer (Mitutoyo) with a resolution of 1 μm. The current was applied between the outer electrodes using a Princeton Analytical Research 363 potentiostat/galvanostat and the resulting potential drop between the inner electrodes was measured with a Keithley 169 multimeter.

The polymer conformation of the electrospun fibers was determined using UV–visible spectroscopy by inserting a microscope glass slide into the path of the polymer jet in front of the copper target for 30 s. The UV–visible spectra of these fibers were measured between 300 and 1100 nm using a Perkin-Elmer Lambda 9 UV–visible–NIR spectrometer. As a comparison between the polymer blend in the solid state and electrospun fibers, the same polymer blend solution was used for electrospinning and also for casting a film onto a microscope glass slide.

3. Results and discussion

3.1. Fiber formation and morphology of electrospun PAn.HCSA / PEO fibers

Without the addition of PEO to PAn.HCSA dissolved in chloroform, no fiber formation occurred, as the viscosity

and surface tension of the solution were not high enough to maintain a stable drop at the end of the capillary tip. Adding more doped polyaniline could not increase the viscosity of the polymer solution, as PAN.HCSA has a very low solubility in chloroform. A stable drop at the end of the capillary tip was achieved once 2 wt.% PEO was added to the solution.

Before any PAN.HCSA/PEO electrospun fibers were produced, PEO was electrospun from chloroform at concentrations between 2 and 4 wt.% to examine the influence of adding polyaniline to the blend on the morphology of the fibers produced. As the potential difference between the capillary tip and the copper plate counter electrode was gradually increased, the polymer solution drop at the end of the capillary tip elongated from a hemispherical shape into a cone shape, that is often referred to as a Taylor cone [5]. Further increasing the applied potential resulted in a jet being initiated near the end of the capillary tip.

The morphology and fiber diameter of the PEO electrospun fibers produced was examined using SEM. For example, the SEM micrograph of the electrospun fibers from a 4 wt.% PEO solution dissolved in chloroform, shown in Fig. 2, revealed that the diameter of the PEO fibers in the

non-woven mat ranged from 950 nm to 2.1 μm , with an average fiber diameter of 1.6 μm . The individual electrospun PEO fibers appear to be randomly distributed in the non-woven mat, and the fibers generally had a slightly varied thickness along the fiber but without the presence of any beads [8]. Although a systematic study to determine the optimal electrical field and concentration for these PEO electrospun fibers with regard to fiber diameter was not completed, it appeared that the thickness of the electrospun PEO fibers was relatively independent of the concentration of the PEO dissolved in chloroform electrospun under these conditions.

The fiber diameter and morphology indicated that the PEO fibers produced were not nanofibers; however, these results are essentially identical to those obtained by Jaeger et al. [9,10] who have extensively studied the electrospinning of PEO fibers from both chloroform and aqueous solutions. They noted that although PEO fibers electrospun from chloroform had larger fiber diameters (1–2 μm) with a uniform thickness, this solvent eliminated the “beads on a string” morphology [9] sometimes found in thinner PEO fibers (200–800 nm) electrospun from aqueous solutions.

Based on these results, we subsequently investigated various ratios of polyaniline and PEO dissolved in chloroform to produce electrospun fibers. The polyaniline in the blend investigated ranged between 11 wt.% (0.5 wt.% PAN.HCSA and 4 wt.% PEO) and 50 wt.% (2 wt.% PAN.HCSA and 2 wt.% PEO). These limits were based on the solubility of PAN.HCSA in chloroform and the minimum concentration of PEO to maintain a stable jet. The experimental conditions successfully used to produce PEO fibers described previously were also used to electrospin the polyaniline/PEO blend fibers. More importantly, the addition of PAN.HCSA to the PEO dissolved in chloroform did not appear to hinder the electrospinning process. As was observed for the electrospinning of PEO fibers from chloroform, the jet was initiated at the end of the capillary tip.

The fiber diameter morphology of the polymer blend electrospun fibers was again examined using SEM. Based on the SEM micrographs for the different PAN.HCSA/PEO blend fibers investigated, these fibers showed a similar fiber diameter and morphology to the PEO fibers described above. For example, the SEM micrograph of the non-woven mat of electrospun fibers from a 2 wt.% PAN.HCSA/2 wt.% PEO solution, shown in Fig. 3, revealed that the fibers in the non-woven mat ranged between 950 nm and 1.9 μm (average fiber diameter, 1.6 μm) with a generally uniform thickness along the fiber. Again the electrospun fibers were distributed randomly in the non-woven mat. From the SEM micrographs of all the different polyaniline/PEO blends electrospun at an electrical field strength of 1 kV/cm, it appears that the addition of PAN.HCSA to the PEO solution has little effect on the diameter of the electrospun fiber. The PAN.HCSA/PEO electrospun fibers produced showed no evidence of any birefringence, thus

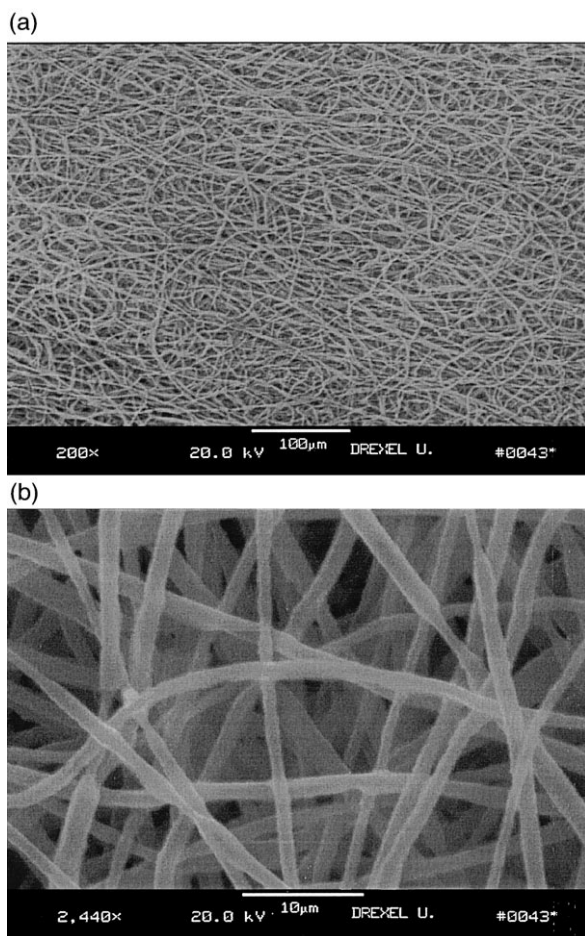


Fig. 2. SEM micrographs of the electrospun fibers from a 4 wt.% PEO solution dissolved in chloroform at 25 kV at (a) 200 and (b) 2440 magnification.

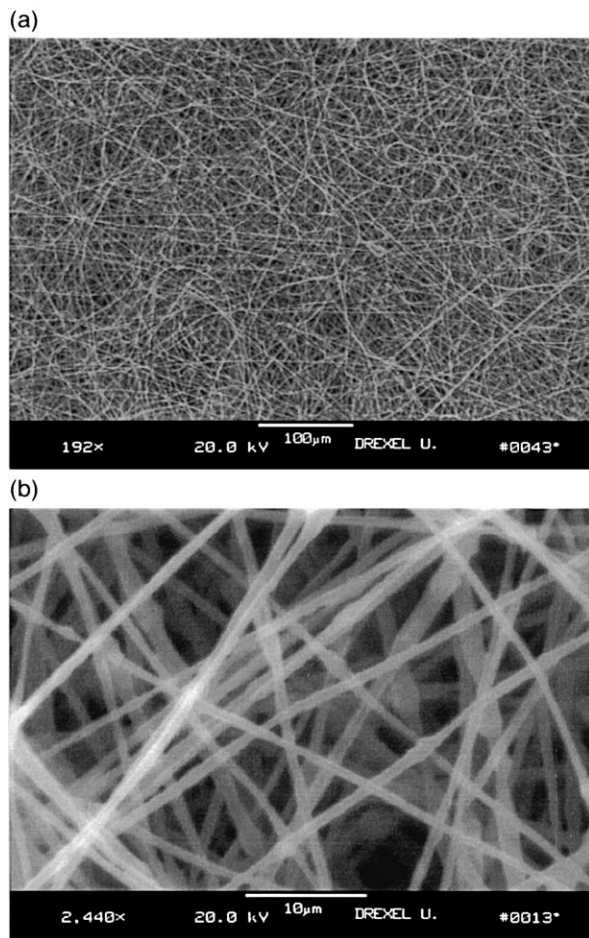


Fig. 3. SEM micrographs of the electrospun fibers from a 2 wt.% PAn.HCSA/2 wt.% PEO solution dissolved in chloroform at 25 kV at (a) 192 and (b) 2440 magnification.

indicating that the polymer chains in the fiber were not oriented with respect to the fiber axis.

3.2. Conductivity of PAn.HCSA/PEO blend films and fibers

Fig. 4 shows the room-temperature conductivity of the PAn.HCSA/PEO electrospun fibers and cast films at various ratios of polyaniline and PEO in the blend. This graph clearly demonstrates that the conductivity of the electrospun fibers in the non-woven mat is significantly lower than that for a cast film at the same polyaniline concentration. This is not an unexpected result as the four-point probe method measures the volume resistivity from which the conductivity can then be calculated and not that of an individual fiber. It must be noted that obtaining the conductivity of the non-woven mat was considerably more difficult than measuring the conductivity of the cast film due to the difficulty in obtaining an accurate thickness measurement on the highly compressible non-woven mat using the micrometer. As can be seen from the SEM micrographs of the electrospun fibers (Fig. 3), the non-woven mat is highly porous and therefore the “fill factor” of the polyaniline fibers is less than that of a cast film. However, it is reasonable to expect that the conductivity of an individual electrospun fiber will be higher than that of the non-woven mat and in fact should be approximately equal to the conductivity of the cast film.

The experimental results for the conductivity of the cast film show similar trends to that observed by Sixou et al. [11] who have extensively studied the conductivity of films cast from NMP solutions of polyaniline doped with trifluo-

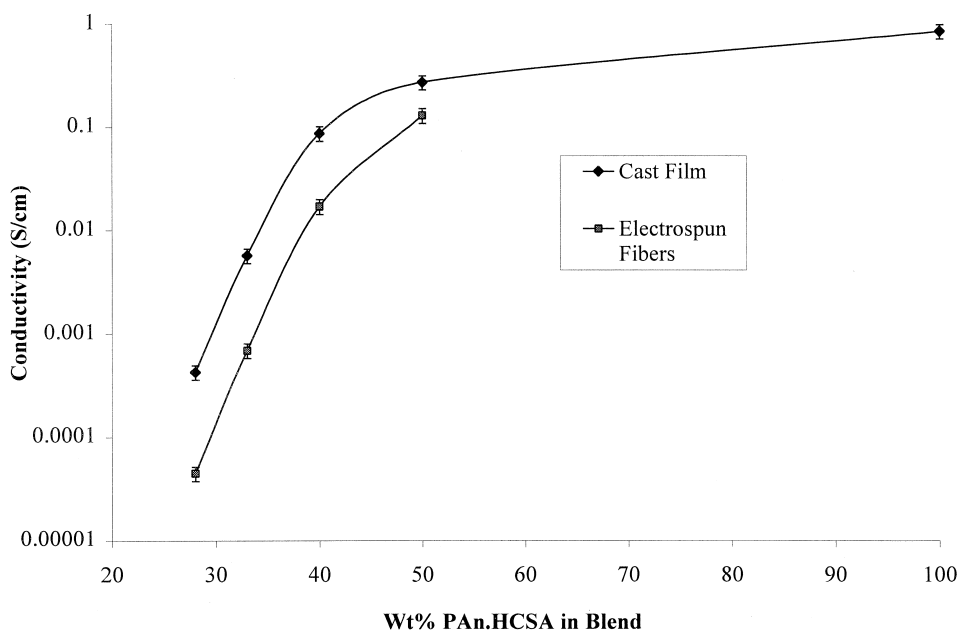


Fig. 4. Electrical conductivity of the PAn.HCSA/PEO blend electrospun fibers and cast films prepared from the same solution.

romethane sulfonimide acid and blended with PEO. Their results suggest that for doped polyaniline blended with PEO, the percolation threshold is approximately 4%, which is significantly higher than the percolation threshold for blends of polyaniline doped with HCSA and poly(methyl methacrylate) (PMMA) or nylon (in both cases less than 1%) prepared from *m*-cresol solvent [12,13]. Although not calculated in the present study, the percolation threshold for the PAn.HCSA/PEO blend is qualitatively consistent with the above study [11]. It is also significantly higher than that of PAn.HCSA blended with PMMA or nylon, which suggests that PAn.HCSA produces a more entangled network in these polymers than in PEO.

3.3. Spectroscopic characterization of PAn.HCSA/PEO blend films and fibers

The UV–visible spectra of different PAn.HCSA/PEO blend films cast onto a glass slide from chloroform after the solution was stirred for 24 h are shown in Fig. 5. The absorption spectra for the different blends show three absorption bands in the visible region, which are consistent with the emeraldine salt form of polyaniline. Both PEO and HCSA have absorption bands only at wavelengths shorter than 300 nm. The position of the two lower wavelength absorption bands at 352 and 430 nm (assigned as the benzenoid/quinoid π – π^* transition and a low wavelength polaron band, respectively) did not change significantly with the concentration of polyaniline in the blend [14]. However, as the concentration of PEO in the blend increased, the position of the high wavelength localized polaron band shifted to lower wavelengths. The position of this band blue-shifted from 793 nm for the pure PAn.HCSA film to 763 nm for the 33 wt.% PAn.HCSA/PEO blend (2 wt.% PAn.HCSA/4 wt.% PEO).

Recently, Zheng et al. [15] have shown that when emeraldine base is doped with HCSA in chloroform to

form a 2-wt.% solution of polymer and dopant, the high wavelength localized polaron band of the PAn.HCSA initially formed, gradually shifts from 730 to 800 nm over 72 h. This shift in the position of the localized polaron band is believed to arise from the slow de-aggregation of the polyaniline chains in solution. With stirring, the aggregated/cross-linked emeraldine base chains [16] gradually becomes disentangled after protonation with HCSA, resulting in a slow conformational change of the polyaniline backbone. This conformational change causes an increase in the conjugation length for the polymer chains, and hence the observed red shift of the localized polaron band. The position of the localized polaron band for the pure PAn.HCSA film is in excellent agreement for the position of this band as determined by Zheng et al. [15] for a film cast from chloroform after 24 h of stirring. However, the red shift of the localized polaron band, as the concentration of PEO in solution is decreased is due to the polyaniline chains becoming entangled with the PEO chains in solution, thus inhibiting the rate of de-aggregation of the polyaniline chains in solution.

MacDiarmid and Epstein [17,18] have proposed that polyaniline can exist in two distinct conformations: the crystalline “extended coil” (highly conducting) conformation and the amorphous “compact coil” (less conducting) conformation. As the above cast films exhibited an intense, well-defined localized polaron band between 760 and 790 nm and no significant near-infrared absorption, this indicates a “compact coil” conformation for the polyaniline chains, which is consistent with the low conductivity observed for the polyaniline/PEO blends.

The UV–visible spectra of different PAn.HCSA/PEO blend fibers electrospun onto a glass slide that was placed just in front of the copper target showed an essentially identical spectra to the cast films prepared from the same solutions (Fig. 5). Both the cast films and the electrospun fibers were prepared after 24 h of stirring, so the position of the absorption bands of the electrospun fibers are directly comparable to those observed in the cast film. The spectra for the electrospun fibers shows a π – π^* transition at 352 nm and a low wavelength polaron band at 420 nm, which are again independent of the PEO concentration. However, as was observed for the cast film, the position of the localized polaron band varied between 766 nm for the 2 wt.% PAn.HCSA/4 wt.% PEO electrospun non-woven mat and 785 nm for the 2 wt.% PAn.HCSA/2 wt.% PEO electrospun non-woven mat.

Absorption spectra of the polyaniline blend electrospun fibers were consistent with those of polyaniline in the emeraldine salt oxidation state and no other absorption bands were observed in the visible region, indicating that the high voltage used in this electrostatic process did not result in any over-oxidation of the polyaniline chains. Over-oxidation causes the degradation of the polyaniline backbone that results in inferior electronic and mechanical properties for the polymer [19].

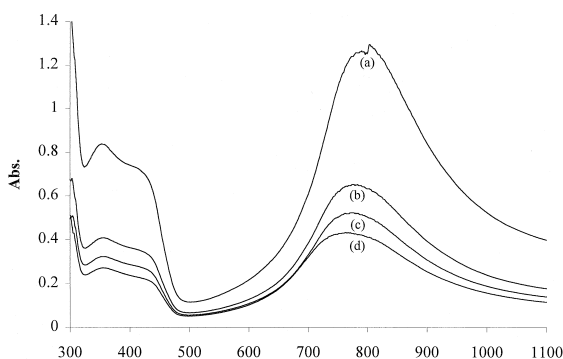


Fig. 5. UV–visible spectra of PAn.HCSA/PEO films cast from chloroform at various PEO concentrations for (a) 2 wt.% PAn.HCSA (pure PAn.HCSA), (b) 2 wt.% PAn.HCSA/2 wt.% PEO, (c) 2 wt.% PAn.HCSA/3 wt.% PEO and (d) 2 wt.% PAn.HCSA/4 wt.% PEO.

3.4. De-doping of electrospun PAn.HCSA / PEO fibers

De-doping of the electrospun PAn.HCSA/PEO fibers could not be achieved by suspending the non-woven mat in 1.0 M ammonium hydroxide aqueous solution since the water dissolved the PEO and caused the fibrous network in the non-woven mat to break apart. Instead, de-doping of the electrospun PAn.HCSA/PEO fibers (11–50 wt.% PAn.HCSA) was achieved by suspending the non-woven mat above the vapor of concentrated aqueous ammonium hydroxide solution. Within 3 s of exposing the non-woven mat to the ammonia vapor, the green non-woven fiber mat turned to blue, indicating that the emeraldine salt in the blend fibers was converted to emeraldine base. Attempts to characterize the emeraldine base/PEO blend fibers by both SEM and UV–visible spectroscopy were unsuccessful, as after the non-woven mat was removed from the ammonia source, the polyaniline in the non-woven mat turned back to the original green color of the as-spun mat. This indicated that emeraldine base in the blend was completely converted back to the conducting emeraldine salt form of polyaniline. The time for this spontaneous re-doping process depended on the ratio of polyaniline to PEO and varied between 3 s for the non-woven mat containing 11 wt.% PAn.HCSA and 7 s for the non-woven mat containing 50 wt.% PAn.HCSA. This extremely high rate of de-doping and spontaneous re-doping occurs at a very much faster rate than for films cast from the same solutions, which occurs on the minute time-scale. This presumably arises from a faster diffusion rate of ammonia vapor into and out of the polyaniline blend fibers, thus stressing the enormous effect an increase in the surface-to-volume ratio accomplished by the ultrafine fibers can have on selected chemical properties of a specific polymer.

4. Conclusions

Conducting ultrafine fibers with diameters less than 2 μm have been successfully produced using the electrospinning process by the blending of the conducting polymer, polyaniline, and PEO, in a wide range of blending ratios. By controlling the ratio of polyaniline to PEO in the blend, fibers having a desired conductivity (comparable to that of PAn.HCSA/PEO cast films) were produced.

The importance of the high surface to volume ratio provided by the electrospun fibers was evident from the at

least one order of magnitude increase in the rate of the vapor phase de-doping and at least two orders of magnitude in the rate of spontaneous re-doping, compared to the cast film.

The successful demonstration of the feasibility of producing electrically conducting blends of polyaniline and PEO in ultrafine fiber form has opened up new functional opportunities for electronic polymers in their doped (metallic) forms.

Acknowledgements

This work was financed jointly by the Office of Naval Research and the Army Research Office under the Multidisciplinary University Research Institute (MURI) program. The authors are grateful to Mr. Wan-Ju Li for his useful discussions and assistance at the beginning of this project.

References

- [1] A. Formhals, US Patent #1,975,504, 1934.
- [2] J. Doshi, D.H. Reneker, *J. Electrostat.* 35 (1995) 151.
- [3] P.W. Gibson, H.L. Schreuder-Gibson, D. Riven, *AIChE J.* 45 (1999) 190.
- [4] F.K. Ko, C.T. Laurencin, M.D. Borden, D.H. Reneker, The dynamics of cell–fiber architecture interaction, in: *Proceedings, Annual Meeting, Biomaterials Research Society, San Diego, April, 1998.*
- [5] D.H. Reneker, I. Chun, *Nanotechnology* 7 (1996) 216.
- [6] I. Chun, D.H. Reneker, H. Fong, X. Fang, J. Deitzel, N.B. Tan, K. Kearns, *J. Adv. Mater.* 31 (1996) 36.
- [7] ASTM Designation: D4496-87, 453.
- [8] H. Fong, I. Chun, D.H. Reneker, *Polymer* 40 (1999) 4585.
- [9] R. Jaeger, M.M. Bergshoeff, C.M.I. Battle, H. Schonherr, G.J. Vancso, *Macromol. Symp.* 127 (1998) 141.
- [10] R. Jaeger, H. Schonherr, G.J. Vancso, *Macromolecules* 29 (1996) 7634.
- [11] B. Sixou, J.P. Travers, C. Barthet, M. Guglielmi, *Phys. Rev. B* 56 (1997) 4604.
- [12] Y. Cao, P. Smith, A.J. Heeger, *Synth. Met.* 55–57 (1993) 3514.
- [13] C.O. Yoon, M. Reghu, D. Moses, A.J. Heeger, Y. Cao, *Synth. Met.* 63 (1994) 47.
- [14] S. Stafstrom, J.L. Bredas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Huang, A.G. MacDiarmid, *Phys. Rev. Lett.* 59 (1987) 1464.
- [15] W. Zheng, Y. Min, A.G. MacDiarmid, M. Angelopoulos, Y.H. Liao, A.J. Epstein, *Synth. Met.* 84 (1997) 109.
- [16] M. Angelopoulos, Y.-H. Liao, B. Furman, T. Graham, *Macromolecules* 29 (1996) 3046.
- [17] A.G. MacDiarmid, A.J. Epstein, *Synth. Met.* 65 (1994) 103.
- [18] A.G. MacDiarmid, A.J. Epstein, *Synth. Met.* 69 (1995) 82.
- [19] P.J.S. Foot, R. Simon, *Phys. D Appl. Phys.* 22 (1989) 1598.