Macromolecular Research, Vol. 10, No. 5, pp 282-285 (2002)

Notes

Continuous Nanofibers Manufactured by Electrospinning Technique

Suck-Hyun Lee* and Jung-Woo Yoon

Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea

Moon Ho Suh

Department of Chemical Engineering, Ajou University, Suwon 442-749, Korea

Received Apr. 8, 2002; Revised July 23, 2002

Abstract : In this paper, we report a modified technique for the production of oriented continuous nanofibers instead of non-woven mats using a rapidly rotating collection device. We are interested in retaining physical properties such as electrical conductivity of fiber bundles in their axial direction. The experiments were performed using polyethylene oxide (PEO) and its blend with polyaniline (PANI). According to the results, a typical fiber with a uniform diameter of about 100 nanometer was produced. The fibers from the PEO/ $CHCl_3$ solution show high crystallinity and good orientation whereas the fibers from the blend solution of PEO/PANI/m-cresol and $CHCl_3$ show no preferred orientation. However, the fibers of the blend exhibit high electrical conductivity of 33 S/cm for a fiber bundle at a PANI level of 50 %.

Keywords : electrospinning, continuous nanofibers, polyethylene/polyaniline blend.

Introduction

Recent studies have shown that the electro-spinning can be a very useful technique for producing ultra-fine fibers with the high surface to volume ratio.[1-4] It provides an interesting route in the making of various functional products such as conducting fibers,[4,6] dressings, scaffold[1] in tissue engineering and high performance filters.[3] The concept of electrostatic spinning was developed in the 1930s[5] and systematic investigations of the process have been carried out recently.[1-6] In this technique, fibers are produced by applying a high electric field between a fiber forming polymer, which may be either in a liquid or melt, and a collecting metallic device. When the electric field overcomes the surface tension of the hanging polymer drop formed at the tip of a capillary tube, a charged jet is ejected. As the jets travel in air towards the collector, fibers are deposited usually in the form of a non-woven fabric.

This study describes electrospinning of nanofibers from polyethylene oxide (PEO) and its blend with polyaniline (PANI). The focus is on nanofiber orientation. In general, oriented polymer nanofibers with functional properties attract considerable interest due to their potential applications. Here a rotating fiber collector to create preferential orientation of nanofibers on the collector was used and a thorough paramertric study of the effects of processing parameters and blend composition on nanofiber and polymer orientation has been made.

Experimental

The polyaniline used in this study is low molecular weight PANI synthesized by a literature procedure[7] and doped with camphorsulfonic acid (CSA). PEO was purchased from Aldrich. It has a weight-average molecular weight of

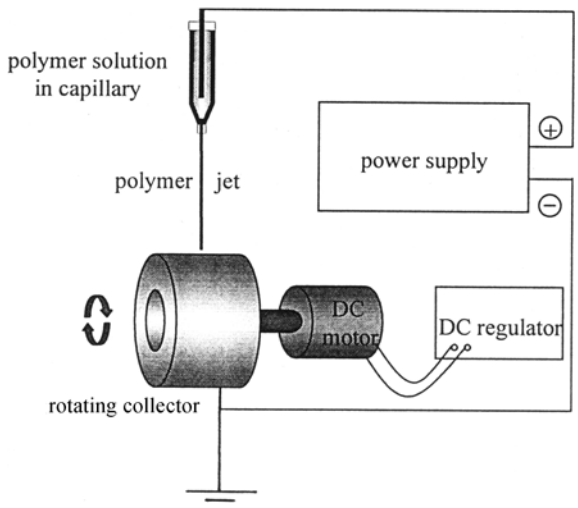

Figure 1. Schematic diagram of the experimental set-up used for electrospinning.

*e-mail : hyja@madang.ajou.ac.kr

300,000. All other chemicals were also purchased from Aldrich. The experimental set-up used for electrospinning is shown in Figure 1. The glass capillary containing polymer solution had a tip diameter of about 0.5 mm. The electric field was provided by a high voltage power supply through a tungsten electrode wire immersed in the spinning dope. During the measurements, the solution in the capillary was at a positive potential and the collecting cylinder was grounded. The electrically charged jet was splayed at the tip of the capillary and collected as a continuous mono-filament on a rapidly rotating cylinder instead of collection screen remaining at rest or slowly moving. The potential difference between the metal electrode and the aluminum sheath on the rotating cylinder as well as the distance between the capillary and collection device varied from 4 to 12 kV for the electrode distance adjusted between 3 and 40 cm. The electric potential and electrode distance were fine-tuned, such that a stable continuous filament was obtained from the capillary tip just before multiple jets took place. The highest wind-up speed above which the thread-line broke depended on various process parameters.

PANI solutions were prepared by mixing the stoichiometric amount of PANI-emeraldine base (EB) and CSA (2 : 1 molar ratio of PhN group to CSA molecule) in a mixed solvent of meta-cresol/$CHCl_3$ (1 : 1, v/v). A polymer blend solution was prepared by dissolving the PEO in a doped PANI solution with a ratio of 50 wt%. These solutions were vigorously stirred to obtain homogeneous solutions and then filtered using a syringe filter of 0.2 μm diameter to remove any particulate material. The morphology and fiber diameters of electro-spun fibers were investigated using atomic force microscopy (AFM). The oriented fibers were aggregated into bundles and adhered to the aluminum sheath, thereby making it difficult to remove fibers from the collecting device in a satisfactory manner. Here we examined the orientation of the fiber bundles by infra red dichroic ratio as well as wide-angle X-ray diffraction patterns. The electrical conductivity of the fiber bundles was measured using four-line probe method [8] with a Keithly237 conductivity measurement unit at dry ambient temperature.

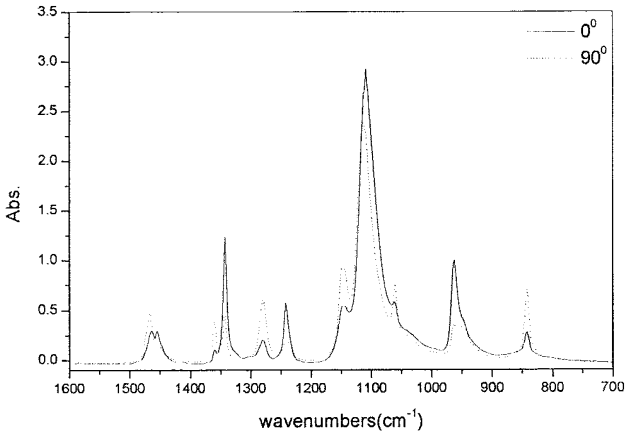

Figure 2. Polarized infrared spectra of polyethylene oxide. The solid (or broken) line represents the spectra measured with the polarized beam with the electric vector parallel (or perpendicular) to the fiber direction.

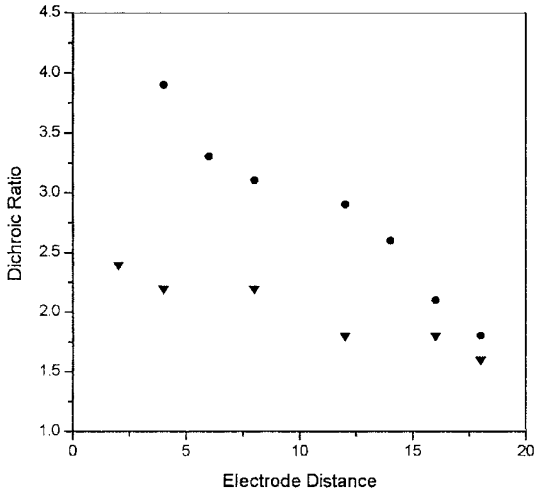

Figure 3. Dichroic ratio as a function of a distance between the capillary tip and the collection device at lower electric potentials: 4 kV (▼), 6 kV(●).

Results and Discussion

The experiments were performed using PEO to obtain a continuous filament by the electrospinning process. As the electric potential is increased, the jet is formed at the capillary tip. Multiple jets were observed when the electric potential and the flow of solution were high. We have adjusted the process parameters to obtain a stable jet for a polymer solution of PEO/$CHCl_3$(2.5 wt%). Once the jet was formed, a continuous filament was wound on a rotating cylinder (diameter 12 cm, height 5.5 cm). To reach a fiber diameter as small as possible, we have changed the distance between the capillary and the cylinder as a function of the electrical potential while keeping the take-up speed at the maximum attainable by our equipment. For the assessment of chain orientation, infrared (IR) dichroism was measured. The dichroic ratio was defined as $R = A_{\parallel}/A_{\perp}$ where $A_{\parallel}$ is the absorbance of the radiation polarized parallel to the fiber axis and $A_{\perp}$ is the absorbance of radiation polarized perpendicular to the fiber axis. Figure 2 shows the polarized FT-IR spectra of an oriented electrospun PEO fiber. To compare quantitatively the dichroic ratio of the fibers, we have chosen a peak around 842 cm^{-1} which arises primarily from anti-symmetric rocking motion of -CH_2.[9] Figures 3 and 4 show the dichroic ratio against the electrode distance for various electrical potentials. The orientation of the fibers increased

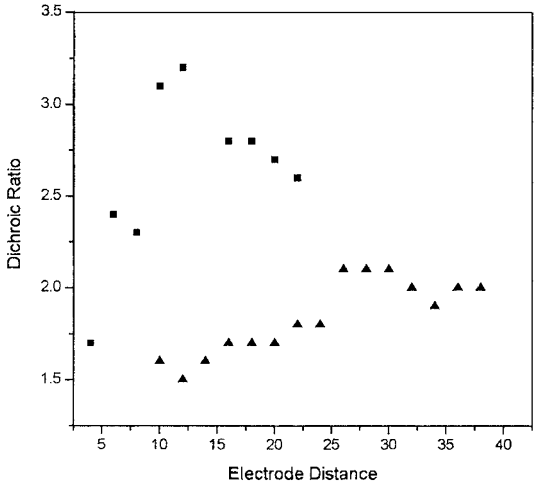

Figure 4. Dichroic ratio as a function of a distance between the capillary tip and the collection device at higher electric potentials: 8 kV (■), 12 kV(▲).

when the collecting cylinder was set to smaller distance from the capillary at relatively low electrical potentials of 4 and 6 kV. As the electrical potential increased to 8 kV, the degree of orientation showed a maximum. For example, the dichroic ratio exhibits a maximal value of 3.3 at a distance of 12.5 cm. However, very little variation of orientation with distance was observed under the electrical potential of 12 kV. These results indicate that the fiber orientation was governed in a complicate manner by the distance and the electrical potential between the capillary and the collecting device. Apparently, the electric field strength between the capillary and the collection device and the solution viscosity are key parameters to produce monofilament. If both the hydrostatic pressure and the applied electric field strength are high, the flow rate through the capillary is high and instability appears at the tip due to the high electric field. When the electrodes were too close, the micro droplets were collected without splaying.

The morphology and fiber diameter of the PEO monofilament produced was examined using AFM. An AFM image of a typical fiber is shown in Figure 5. It reveals that the fiber has a smooth surface with a fairly uniform diameter of about 100 nm without any noticeable beads on a string. Although we did not perform a systematic study to determine optimum take-up speed against fiber diameter for these PEO systems, the fiber diameter tended to decrease significantly with increasing the rotating speed of the collection cylinder. The minimum value of the fiber diameter of 60 nm attained with a speed of 1,350 m/min should be considered as an upper limit at this time. These results are encouraging since the PEO fibers produced in non-woven mat were not nano-fibers: Jaeger *et al*.[10] and Norris *et al*.[4] have recently reported that PEO fibers electrospun from chloroform had larger fiber diameters (1-2 μm). Figure 6(a) shows the WAXS diagram of the fiber bundle spun from $CHCl_3$ solution at a take-up speed of 1,130 m/min. The diffraction pattern indicates that the sample is well oriented. The degree of orientation estimated by measuring the angle of the arcs is approximately 16-22°. This orientation value is considered to be high for an electrospun fiber bundle.

The electrospinning of continuous fibers from doped PANI/ $CHCl_3$ solution was not possible. The conducting form of PANI/CSA was only slightly soluble in $CHCl_3$. The viscosity and surface tension were not high enough to form a stable jet. Thus, we attempted to make a blend of PANI/PEO to fit in with the electrospinning range. In order to simplify the rather complex electrospinning technique, the blending ratio of the PANI was fixed to be 1/1 by weight and the mixed solvent of m-cresol/$CHCl_3$ (1/1 by volume) was used to obtain a polymer solution (4 wt%). Note that the type and the mixed composition of the solvent may have an important influence on the conductivity of PANI fibers but it is not our main concern in this study. On the basis of our electrospinning experience on PEO we have produced

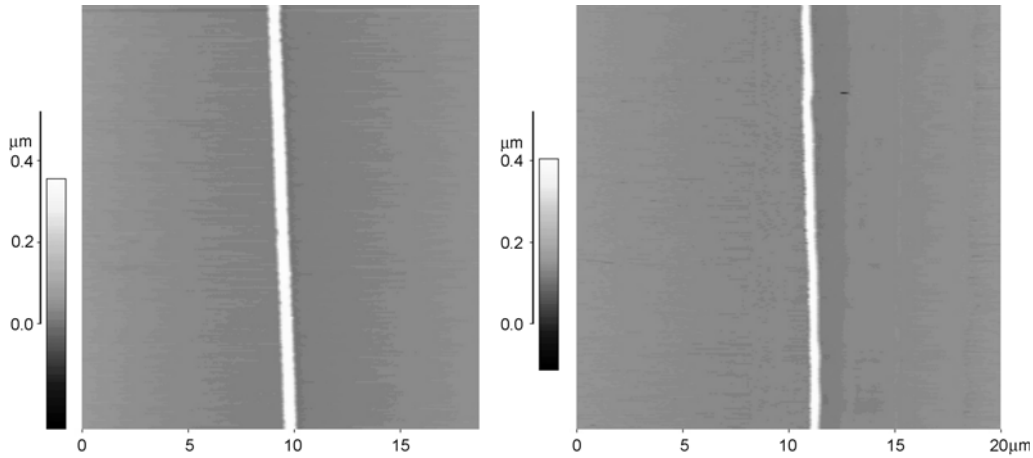

Figure 5. AFM micrographs of electrospun fibers from a 2.5 wt % PEO solution dissolved in chloroform.

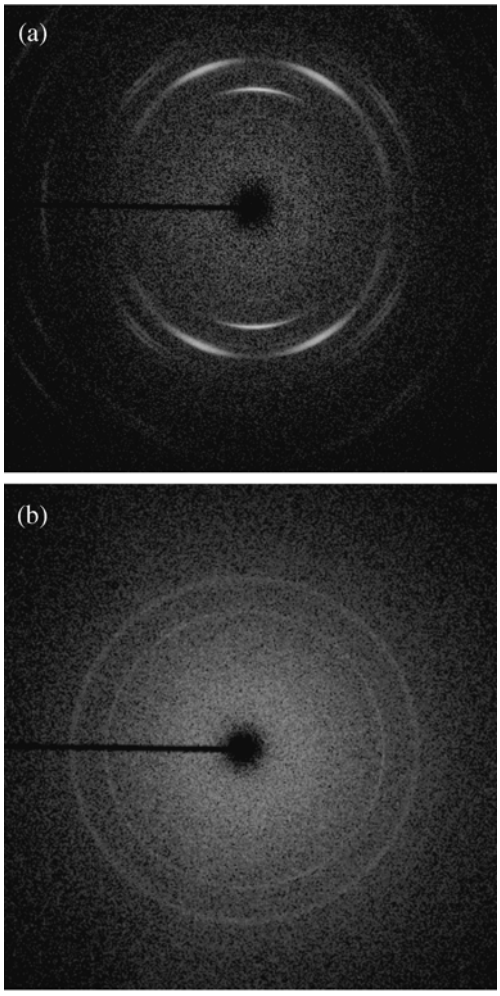

Figure 6. WAXS pattern obtained for as-spun fibers from the solutions of (a) PEO/$CHCl_3$ and (b) PEO/PANI blend (1 : 1 wt ratio)/ *m*-cresol/$CHCl_3$.

the continuous filament of a PANI/PEO blend similar to the PEO sample. A typical WAXS diagram from a sample prepared at 6 kV and the electrode distance of 2 cm is shown in Figure 6(b). The X-ray pattern consists only of two weak rings centered at ca. d ~4-5Å. Thus the fibers of the blend are neither well oriented nor highly crystalline although a significant amount of oriented amorphous scattering is seen in the pattern.

The electrical conductivity of the fiber bundle measured in a direction parallel to the fiber axis by the four-probe method was revealed to be about 33 S/cm. This conductivity value is surprisingly high for a fiber bundle at a PANI level of 50%. With refinement of the processing parameters and fiber post-treatment to improve fiber collection, one should be able to produce nanofibers having an additionally improved conductivity. It will be also interesting to see that the fibers retain much of the tensile properties of the PEO by investigating the mechanical properties of the monofilament.

In summary, electrospinning has been used to produce continuous nanofibers from the polymer solutions of PEO and its blend with PANI. The spinning apparatus was designed so that a continuous monofilament could be obtained instead of non-woven mats. The resultant fibers have smooth surfaces with uniform diameters less than 20 nm. The WAXS and dichroic measurement indicated that the PEO fibers are partially crystalline and well oriented but the PANI/PEO fibers show low crystallinity with no preferred orientation. The m-cresol/$CHCl_3$ solution of a PANI/PEO/CSA salt produces electrospun fibers having a high electrical conductivity.

Acknowledgements. We thank financial support by Korea Science and Engineering Foundation through Hyperstructured Organic Materials Research Center.

References

(1) J. Doshi, *The Elecrospinning Process and Applications of Electrospun Fibers*, Ph.D. Thesis, University of Akron, Akron, OH, 1994.
(2) H. Jaeger, H. Schonherr, and G. J. Vansco, *Macromolecules,* **29**, 7634 (1996).
(3) P. W. Gibson, H. L. Schreuder-Gibson, and D. Riven, *AIChE J.*, **45**, 190 (1990).
(4) I. D. Norris, M. M. Shaker, F. K. Ko, and A. G. MacDiarmid, *Synth. Met.*, **114**, 109 (2000).
(5) A. Formhals, US Patent 1,975,504 (1934).
(6) D. H. Reneker and I. Chun, *Nanotechnology,* **7**, 216 (1996).
(7) A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Sonasiri, and A. J. Epstein, *Conducting Polymers*, L. Alcacer, Ed., Dordrecht, 1987, pp 105.
(8) ASTM Designation: D4496-87; 453.
(9) T. Yoshihara, H. Tadokoro, and S. Murahashi, *J. Chem. Phys.*, **41**, 2902 (1964).
(10) R. Jaeger, M. M.Bergshoef, C. M. I. Batlle, H. Schonherr, and G. J. Vansco, *Macromol. Symp.,* **127**, 141 (1998).