Fundamental Parameters Affecting Electrospinning of PAN Nanofibers as Uniaxially Aligned Fibers

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Received 13 July 2005; accepted 12 February 2006
DOI 10.1002/app.24290
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electrospinning with a collector consisting of two pieces of electrically conductive substrates separated by a gap has been used to prepare uniaxially aligned PAN nanofibers. Solution of 15 wt % of PAN/DMF was used tentatively for electrospinning. The effects of width of the gap and applied voltage on degree of alignment were investigated using image-processing technique by Fourier power spectrum method. The electrospinning conditions that gave the best alignment of nanofibers for 10–15 wt % solution concentrations were experimentally obtained. Bundles like multifilament yarns of uniaxially aligned nanofibers were prepared using a new simple method. After-treatments of these bundles were carried out in boiling water under tension. A comparison was made between the crystallinity and mechanical behavior of posttreated and untreated bundles.
 J Appl Polym Sci 101: 4350–4357, 2006

Key words: electrospinning; polyacrylonitrile; aligned nanofibers; bundle;

INTRODUCTION

Electrospinning is a straightforward method that relies on electrostatic forces to produce fibers with submicron diameter from polymer solutions or melts. In a typical process, an electrical potential is applied between a droplet of polymer solution, or melt, held through a syringe needle and a grounded target. Electrostatic charging of the droplet results in the formation of the well-known Taylor cone. When the electric forces overcome the surface tension of the droplet from the apex of the cone, a charged fluid jet is ejected.[1] The jet exhibits bending instabilities due to repulsive forces between the surface charges, which is carried with the jet, and follows a looping and spiraling path.[2,3] The electrical forces elongate the jet thousands of times and the jet becomes very thin. Ultimately, the solvent evaporates, or the melt solidifies and very long nanofibers are collected on the grounded target.[1] The fiber morphology is controlled by the experimental design and is dependent on solution conductivity,[4,5] solvent polarity,[5] solution concentration,[4] polymer molecular weight,[6] viscosity[4] and applied voltage.[7]

Because of the chaotic oscillation of the electrospinning jet the nanofibers are obtained in nonwoven form, which are used in many applications such as filtration,[8] tissue scaffolds,[9] wound dressing,[10] and drug delivery.[11] Some applications (e.g., carbon nanofibers from electrospun PAN nanofibers precursor) require well-aligned and highly ordered nanofibers. To prepare carbon nanofibers, the precursor PAN nanofibers need to undergo a series of heat treatments. The PAN precursor nanofibers are initially oxidized under tension and then carbonized in an inert atmosphere. The electrospun webs are difficult to handle (webs are very delicate, randomly aligned, and are amorphous) and it is difficult to keep the nanofibers in this form under tension during stabilization. As a result carbon nanofibers with poor mechanical properties are expected from these precursor nanofibers. Also in general, higher degree of molecular orientation in the original PAN precursor fiber results in carbon fibers with better mechanical properties particularly the tensile modulus.[12] If one can prepare well-aligned and highly ordered PAN nanofibers precursor, then that could lead to higher molecular orientation and degree of crystallinity and as a result better mechanical properties during after-treatment of nanofibers.

Fennessey and Farris prepared tows of unidirectionally and molecularly oriented PAN nanofibers using a high speed, rotating take-up wheel. The aligned tows were twisted into yarns, and the mechanical properties of the yarns were determined as a function of twist angle. Their yarn with twist angle of 11° had initial modulus and ultimate strength of about 5.8 GPa and 163 MPa, respectively.[12] Deitzel et al. have obtained yarns of aligned poly(ethylene oxide) nanofibers by introducing an electrostatic lens element to stabilize

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the liquid jet.[13] Zussman and coworkers have demonstrated the use of a wheel-like bobbin as the collector to position and align individual nanofibers into parallel arrays.[14] Tan et al. reported the use of a metal frame as the collector to generate parallel arrays of polycaprolactone electrospun ultrafine fibers and then examined the tensile properties of a single strand of these fibers.[15]Li et al. demonstrated the use of electrospinning as a simple and versatile method for generating nanofibers as uniaxially aligned arrays over large areas by means of an electrostatic interaction between electrostatic field and charged nanofibers. The abovementioned method is basically the same as the conventional electrospinning method that used a collector consisting of two pieces of electrically conductive substrates separated by a gap. The width of this gap could be varied from hundreds of micrometers to several centimeters. The electric field lines in the vicinity of the collectors were split into two fractions pointing and pulling the two ends of the fiber toward the two collectors and stretch the nanofiber across the gap. This process could be repeated and arrays of uniaxially aligned nanofibers could be collected over large areas. By using this method, nanofibers with the length from hundreds of micrometers to several centimeters and diameters ranging from tens of nanometers to several micrometers could be prepared as uniaxially aligned arrays.[16,17] Their study showed that the degree of alignment of the nanofibers increased with collection time but the effects of width of gap and applied voltage were not studied quantitatively in the literature. The aims of this work were first to study the effects of width of gap and applied voltage on the degree of alignment of nanofibers, density of aligned nanofibers and proportion of aligned nanofibers mass to the all and alignment of nanofibers was analyzed using digital image-processing technique by Fourier power spectrum method. Then to obtain the electrospinning conditions that gave the best alignment of PAN nanofibers for 10–15 wt % concentrations. Finally to compare crystallinity and mechanical behavior of posttreated and untreated bundles of uniaxially aligned nanofibers.

EXPERIMENTAL

Materials

Industrial polyacrylonitrile (PAN) was received from Iran Polyacryle and dimethylformamide (DMF) was obtained from Merck, as polymer and solvent. The weight average molecular weight ($\overline{M_w}$) and the number average molecular weight ($\overline{M_n}$) of the received PAN were $\overline{M_w}$ = 100,000 g/mol and $\overline{M_n}$ = 70,000 g/mol. The polymer and solvent were dried before use and the 10–15 wt % solutions of PAN in DMF were prepared.

Electrospinning setup

The electrospinning apparatus consists of a syringe pump, syringe needle, high voltage power supply and a grounded collector, which was fabricated by two pieces of aluminum foil strips separated by an insulating gap. Each solution was loaded into a syringe and positive electrode was clipped onto the syringe needle with 0.7 mm diameter. The flow rate of the polymer solution to the needle tip was maintained so that a pendant drop remains during electrospinning. Solutions were electrospun horizontally onto the target.

Microscopy

Electrospun nanofibers were observed by scanning electron microscopy (SEM) and optical microscopy. The diameters of these nanofibers were quantitatively measured from their SEM images with high magnification. A Motic optical microscope was used to capture images for alignment analysis. All nanofibers were dried at ~70°C in an oven for ~2 h prior to observation.

Analysis of fiber alignment

Fiber alignment was analyzed using image-processing technique by Fourier power spectrum method (FPSM). This method has been used to evaluate the orientation of fibers on the texture, i.e., mat and nonwoven. One of the features which is used with the FPSM is the angular power spectrum (APS), $A(\theta)$, which contains directionality information on texture.[18]

$$A(\theta) = \sum_{r=1}^{R} P_r(\theta) \quad (1)$$

where P is a two-dimensional power spectrum for an $N \times N$ image picture, and r (varied from 1 to R) and (θ) (varied from 0 to π) are the variables in the polar coordinate system. R is typically chosen as $N/2$.

The two-dimensional power spectrum function $P(u, v)$ was calculated as follows.

$$P(u,v) = |F(u,v)|^2 \quad (2)$$

For $u, v = 0,1,2,\ldots, N-1$, here $F(u, v)$ are two-dimensional Fourier transforms of the image.

All images used in the process were obtained using the Motic optical microscopy at a resolution of 480 × 480 pixels in 400× magnifications.

After-treatments of nanofibers

After-treatments of nanofibers were carried out in boiling water (about 94°C) for 10 min with the bundle under tension and then were dried at 110°C.

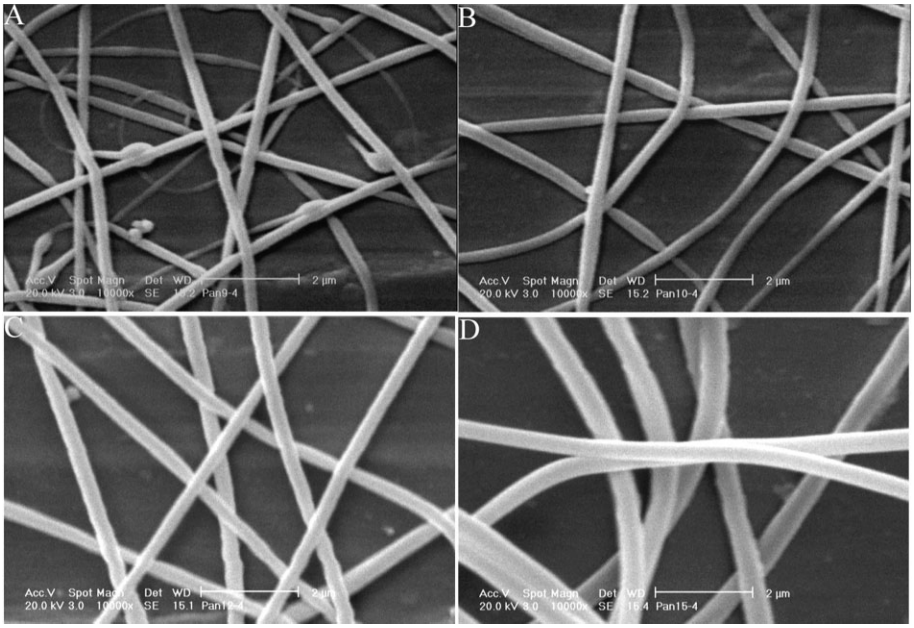

Figure 1 SEM images of electrospun PAN nanofibers. Concentrations: (A) 9 wt %; (B) 10 wt %; (C) 12 wt %; (D) 15 wt %.

X-ray diffraction

Wide angle X-ray diffraction (WAXD) patterns were obtained for bundles of untreated and treated nanofibers on a Philips system using Ni-filtered Cu Kα radiation. The diffraction scans were collected at $2\theta = 10 - 35°$ and a background were subtracted. Calculation of crystallinity index (CI) was done according to Bell and Dumbleton method[21] by the extrapolation of crystalline and amorphous part of the diffraction pattern.

Mechanical testing

The mechanical behaviors of dried bundles of uniaxially aligned PAN nanofibers were examined using the Zwick 1446–60 with a crosshead speed of 30 mm/min and gauge length of 30 mm under standard conditions. The average linear density of the bundles was all 60 den. The E-modulus, stress and strain of samples were determined.

RESULTS AND DISCUSSION

Electrospinning of nanofibers

A series of experiments were carried out using different concentrations of PAN/DMF solutions. SEM images of electrospun PAN nanofibers with different concentrations are shown in Figure 1. By using 8 wt % concentration, regardless of the electrospinning voltage, the polymer solution did not form nanofibers but fine droplets were formed falling on the collecting target. At 9 wt % concentration, nanofibers with average fiber diameter of about 155 $\pm$ 40 nm were formed, but a few beads were seen. By increasing the concentration to 10 wt %, the morphology of nanofibers was changed from a beaded fiber to a uniform fiber structure and the fiber diameter was increased slightly to 165 $\pm$ 25 nm. Therefore maintaining a minimum concentration of polymer solution was critical to electrospin uniform PAN nanofibers with extensive chain entanglement. In electrospinning, by elongation flow of the fluid jet, the coiled macromolecules in solution are transformed into oriented entangled networks that persist in the solidified fiber. Below this critical concentration of 10 wt % in this work, chain entanglements appear to be insufficient to stabilize the fluid jet and by contraction of the diameter of the jet, due to the surface tension, beads or beaded nanofibers were formed. At higher concentrations, viscoelastic forces which prevented rapid elongation and changes in fiber shape resulted in uniform fiber formation. By increasing the concentration to 15 wt %, uniform fiber structure was obtained. On the other hand by increasing the polymer solution concentration, the fiber diameter was also gradually increased to about 400 $\pm$ 40. At above 15 wt % concentration, due to the cohesive nature of the solutions, controlling and maintaining the flow of the polymer solution from the tip of the syringe needle was hard and therefore no consistent electrospinning was proceeded.

Electrospinning of uniaxially aligned nanofibers

In the case of electrospinning, the as-spun nanofibers are highly charged. Since the initial movement is

caused by the bending instability of a charged jet, the direction of as electrospun nanofibers is randomized. After the fiber has been ejected, its motion is mainly controlled by three types of electrostatic forces exerted by the strong external field, the collector and any adjacent charged nanofibers, respectively. When a grounded conductive plate is used as the collector, these electrostatic forces will have no preferential direction in the plane of the collector, and there will be no order in the collected nanofibers. When an insulating gap is introduced into the collector, it changes the structure of the external electric field. As a result, the directions of the electrostatic forces acting on the fibers, which are sitting across the gap, will be altered. Both the width of the gap and the applied voltage can change these forces and consequently the alignment of nanofibers.

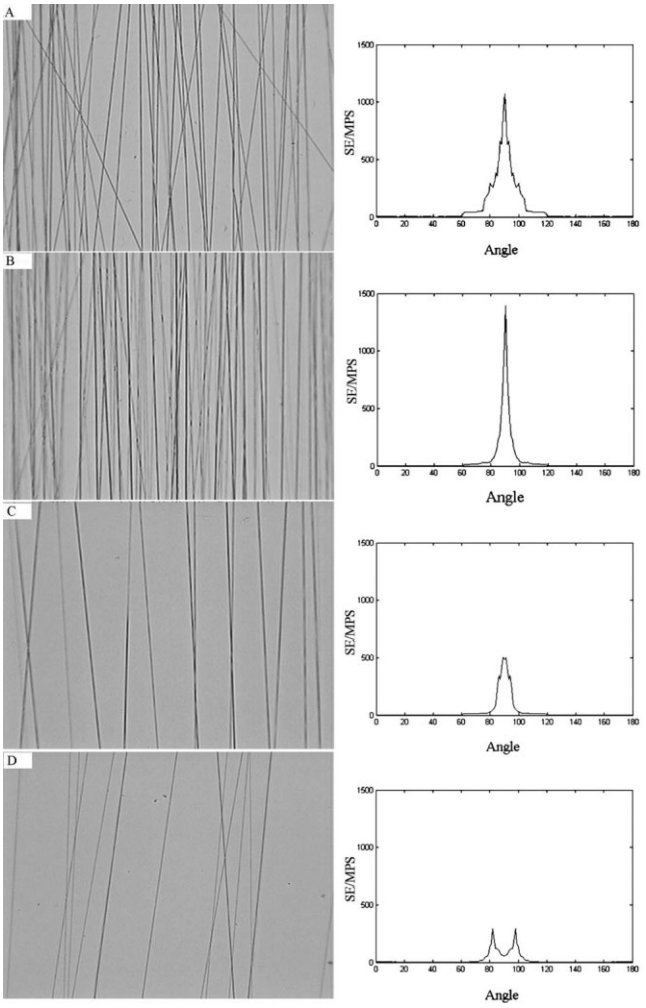

Figure 2 Optical micrograph of electrospun PAN nanofibers with corresponding normalized APS. Concentration: 15 wt %. Voltage: 11kV. Widths of gap: (A) 2 cm; (B) 3 cm; (C) 4 cm: (D) 5 cm.

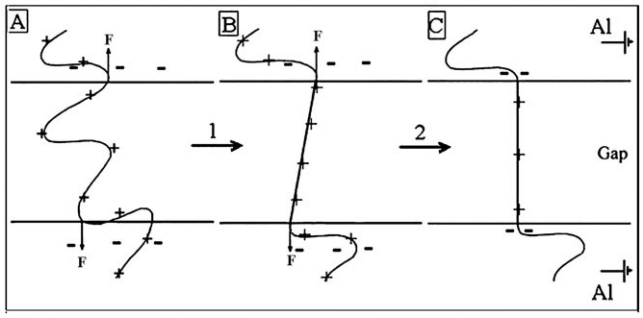

Figure 3 Schematic illustration of the process that aligned nanofibers.

The effect of width of gap on the alignment of nanofibers

The nanofibers which have been stretched across the gap are aligned and their length is as long as the width of the gap. The width of the gap could be varied from hundreds of micrometers to several centimeters, but to change the widths of the gap, there are some limitations. Therefore, to investigate the effect of width of the gap in alignment of nanofibers, electrospinning experiments from 15 wt % PAN/DMF solution were carried out and the width of the gap was varied from 2 to 5 cm. Figure 2 shows optical micrograph of electrospun nanofibers with their corresponding normalized APS (SE/MPS: ratio of intensity of the APS to the corresponding mean intensity of the Fourier power spectrum). The sharpness of the peak at an angle $\pi/2$ on the APS shows degree of alignment of nanofibers on the vertical direction and area of that peak shows density of aligned nanofibers. The APS shows that by increasing the width of gap from 2 to 5 cm, the density of aligned nanofibers decreases. But the best alignment of the nanofibers was obtained with 3 cm width of gap.

If the as-spun charged nanofibers are affected by pulling forces, then they can be aligned. This alignment process can be divided into two steps. Figure 3 shows schematically these steps. Electrostatic forces that are resulted from the electric field and the Coulomb interactions between the positive charges on the nanofiber and the negative image charges on the two grounded collectors will pull the two ends of the fiber toward the two collectors and consequently make the fiber straight. With this pulling forces continuing, the fiber turns perpendicularly toward the edges of the collectors. Then the two ends of the fiber are deposited on the collectors. The two ends of the fiber and the nanofibers that are directly deposited on the top of a collector can immediately be discharged. But those nanofibers that are stretched across the gap will remain highly charged after the deposition. This process could be repeated. Now if these steps are being completed for all upcoming nanofibers, then arrays of

TABLE I
Proportion of Aligned Nanofibers Mass to the All Electrospun Nanofibers

Width of gap (cm)	Aligned nanofibers (mass %)
2	15
3	20
4	12
5	9

uniaxially aligned nanofibers will be collect over large areas across the gap. In the case of 2 cm width, the above-mentioned steps did not get completed for some nanofibers, therefore some nanofibers were deposited at some angles. Consequently their APS does not show sharp peak. By increasing the width further to 3 cm, the aforementioned 2 steps got completed for most of the collected nanofibers, therefore the highest alignment of the nanofibers were resulted.

To obtain proportion of aligned nanofibers mass to the all electrospun nanofibers, we weighed the aligned nanofibers and the all electrospun nanofibers separately and obtained the percentage of aligned nanofibers. The results are shown in Table I. With 2 cm width, aligned nanofibers density was at maximum. But since we were collecting the shortest nanofibers length, it did not have the maximum mass percent. By increasing the width, aligned nanofibers length increases, but the density decreases. In this work, 3 cm width appeared to be the optimum condition and 20% aligned nanofibers mass was obtained.

The effect of voltage on the alignment of nanofibers

In a series of experiments, the applied voltage was varied from 10 to 13 kV while the concentration and the width of gap were kept constant at 15 wt % and 3 cm, respectively. Electrospinning jet started forming from 8.5 kV, but electrostatic forces were not strong enough to form continuous jet from the tip of the syringe needle. Then we began electrospinning from 10 kV and the jet remained continuous. Figure 4 shows images of some of the electrospun nanofibers that were spun under these conditions and their corresponding normalized APS. It can be seen that the degree of alignment of nanofibers increased from 10 to 11 kV and then decreased by increasing the voltage. Therefore 11 kV appeared to be the best voltage in these experiments and highest alignment of nanofibers resulted.

The effects of voltage observed in the previous experiments may be related to the "whipping" instability. The most important element operating during electrospinning is the rapid growth of a nonaxisymetric, or whipping instability that causes bending and allows the electrical forces to elongate the jet.[19] Increasing the applied voltage, increases whipping instability and consequently increases the as-spun nanofibers entanglement which makes alignment of nanofibers more difficult, but on the other hand increases the acting forces which attempt to align the nanofibers. At 13 kV and above, the as-spun nanofibers got entangled with each other. When the acting forces try to pull the two ends of the fiber towards the two collectors to align them, some of the nanofibers get entangled and knotted as can be seen in Figure 4(D), therefore that is why alignment of nanofibers was not satisfactory at 13 kV and above.

The effect of concentration

To produce uniaxially aligned nanofibers of different diameters, the electrospinning conditions that gave the best alignment of nanofibers for 10–15 wt % con-

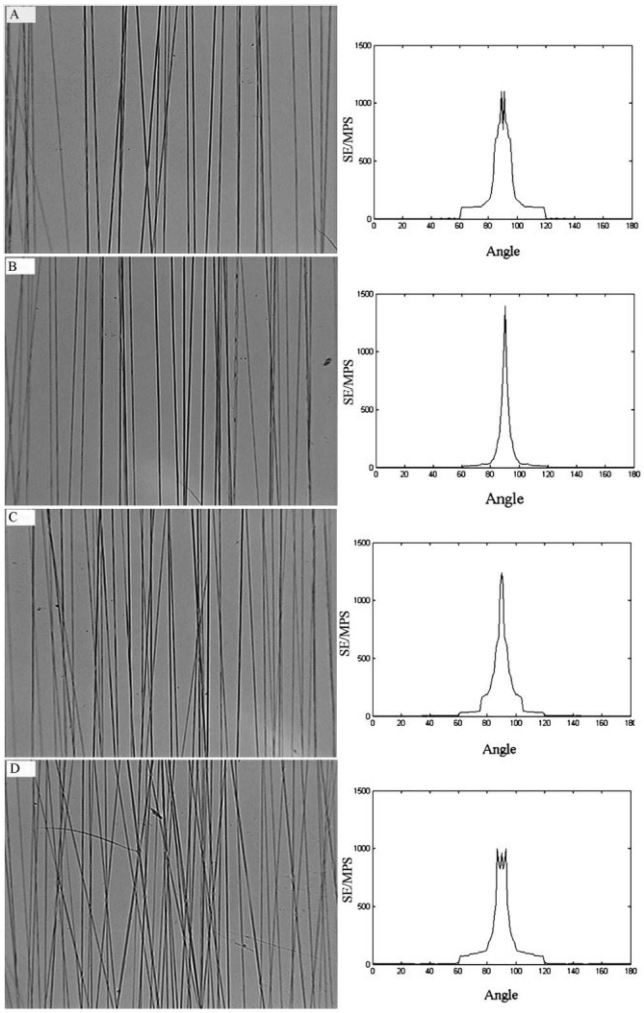

Figure 4 Optical micrograph of electrospun PAN nanofibers with corresponding normalized APS. Concentration: 15 wt %. Widths of gap: 3 cm. Voltage: (A) 10 kV; (B) 11 kV; (C) 12 kV: (D) 13 kV.

TABLE II
The Electrospinning Conditions That Gave the Best Alignment of the Nanofibers

Concentration (wt %)	Tip to target distance (cm)	Voltage (kV)	Width of gap (cm)	Fibers diameter (nm)
10	15	9	1	165 ± 25
11	15	9	1.2	205 ± 25
12	20	9.5	1.5	245 ± 20
13	20	10	2.2	255 ± 30
14	20	11	2.5	300 ± 30
15	20	11	3	400 ± 40

centrations were experimentally obtained; these conditions are shown in Table II. Figure 5 shows SEM images of electrospun nanofibers produced under these conditions that gave the best alignment. For example, nanofibers with average diameter of 245 ± 20 nm were obtained from 12 wt % concentration. In this concentration the width of the gap and voltage that gave best alignment were 1 cm and 9 kV, respectively. As the average diameters of nanofibers decreased from 400 to 245 nm, lower voltages were needed to align them, but on the other hand the alignment process was so difficult that consequently lower nanofibers lengths were obtained. Results show that the uniaxially aligned nanofibers obtained by this method, had the aspect ratio (l/d) of higher than 5000. Such high aspect ratios (l/d) of aligned nanofibers make them very interesting for some applications

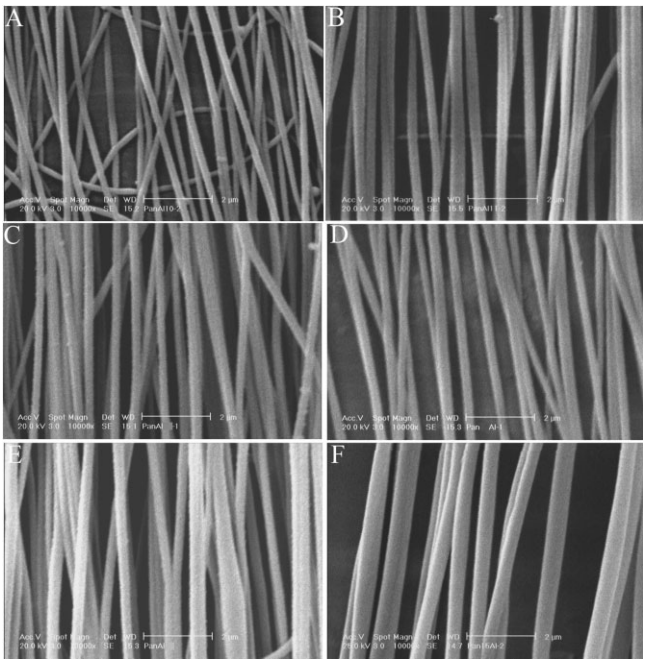

Figure 5 SEM images of electrospun uniaxially aligned PAN nanofibers. Concentrations: (A) 10 wt %; (B) 11 wt %; (C) 12 wt %; (D): 13 wt %; (E) 14 wt %; (F) 15 wt %.

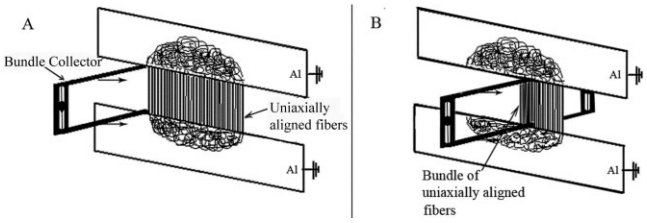

Figure 6 (A) The bundle collector was put vertically at the end point of the gap. (B) The bundle collector was moved across the gap to another side for depositing bundle of uniaxially aligned nanofibers.

such as carbon nanofibers precursor for reinforcing composites.

Preparation of bundle of uniaxially aligned nanofibers

Bundles of uniaxially aligned nanofibers were prepared using a new simple method. Figure 6 shows schematically the set up of this method. At first, using optimum condition, uniaxially aligned nanofibers were electrospun over a comparatively large area. After that a collector like a frame was used to deposit the nanofibers stretched across the gap (the width of the collector was equal to the width of the gap). Then the collector was put vertically at the end point of the gap [Fig. 6(A)], next the collector was moved across the gap to another side [Fig. 6(B)]. Finally, bundle of uniaxially aligned nanofibers were deposited by the collector. Figure 7 shows typical SEM image of bundle of uniaxially aligned PAN nanofibers that was produced using a 15 wt % PAN/DMF solution concentration with the width of gap of 3.5 cm. The lengths of the bundles were 3 cm, which is ~85% of the width of the gap between the collectors.

X-ray characterizations

Posttreatments of nanofibers were carried out in boiling water while the bundle was under tension and then were dried. Figure 8 shows WAXD patterns that were obtained for the bundles of untreated and posttreated uniaxially aligned nanofibers. As reported by Deitzel et al. and Zong et al. earlier,[13,20] electrospinning retards the crystallization process of semicrystalline polymers. In this work, similar behavior was observed in electrospun PAN nanofibers. In the case of posttreated bundle, a strong peak at $2\theta = 17.2°$ corresponding to a spacing of $d \approx 5.1$ Å from the $10\,\bar{1}0$ reflection and a weak peak at $2\theta = 29.8°$ corresponding to a spacing of $d \approx 3$ Å from the (1120) reflection. Whereas in the case of untreated bundle, the main crystalline peak at $2\theta = 17.2°$ is very broad and the crystalline peak at $2\theta = 29.5°$ is absent. The equatorial peaks at $2\theta = 29.5°$ and $2\theta = 17.2°$ are common to the

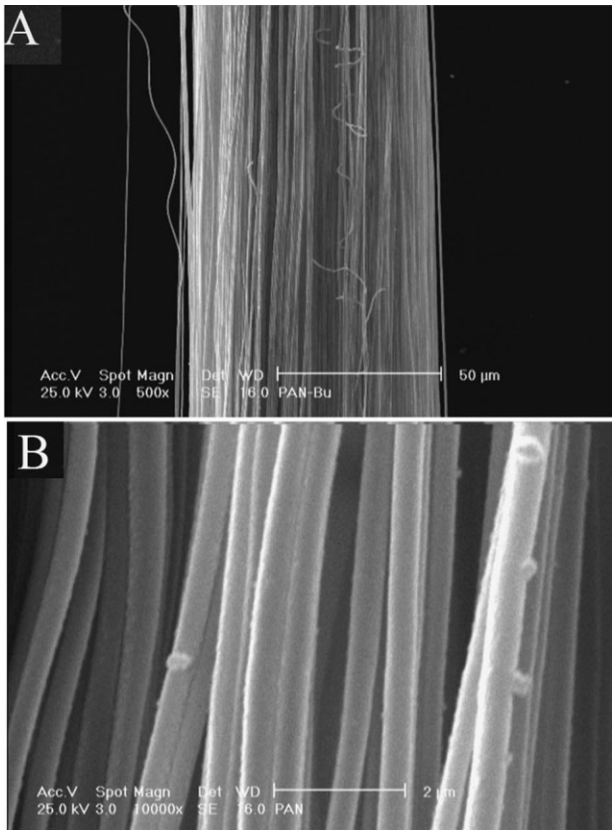

Figure 7 (A) SEM image of a typical bundle of uniaxially aligned PAN nanofibers, forming a multifilament yarns. (B) High magnification SEM image of the nanofibers in this bundle.

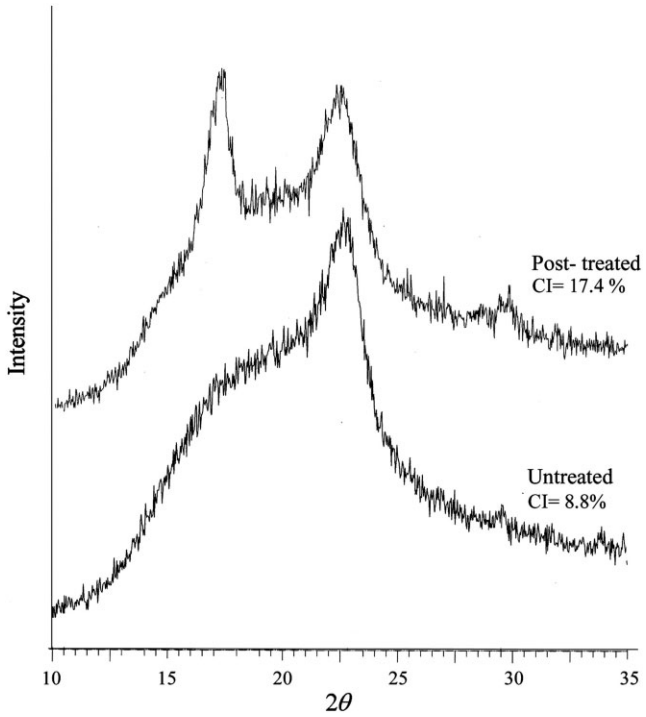

Figure 8 WAXD patterns of the bundles of untreated and posttreated uniaxially aligned nanofibers.

fiber diffraction pattern of PAN with hexagonal packing.[12] This finding appears to confirm that crystallization was retarded during electrospinning, which could be attributed to the rapid solidification of the stretched polymeric chains at high elongation rates during the later stages of electrospinning that significantly hindered the formation of crystals. In other words, the polymer chains did not have enough time to organize into 3D ordered crystal structures before they were solidified. Therefore posttreated bundle had CI of 17.4% much higher than CI of 8.8% for untreated bundle. Since the T_g of the PAN polymeric fibers is in the range of 75°C, so in boiling water, the molecular mobility appeared to be enough to permit some additional development of crystalline order and on the other hand the polymeric chains had sufficient time to organize themselves into more arranged crystal structure.

Mechanical characterizations

A comparison was made between the mechanical properties of the bundles of untreated and posttreated uniaxially aligned PAN nanofibers. The stress–strain curves of these samples are shown in Figure 9. Also the values of some parameters for quantitative comparisons are summarized in Table III. The values of E-Modulus and tensile strength at break increase from 2786 ± 200 MPa and 99 ± 12 MPa (0.92 g/den) to 4575 ± 220 MPa and 178 ± 15 MPa (1.62 g/den) for untreated and posttreated bundles respectively, whereas the elongation at break of the posttreated bundle was found to decrease significantly. In other words, the bundle became much stronger but relatively with lower elongation after the posttreatments, which could be attributed to the increase in the degree of crystallinity for posttreated sample. However, yet the

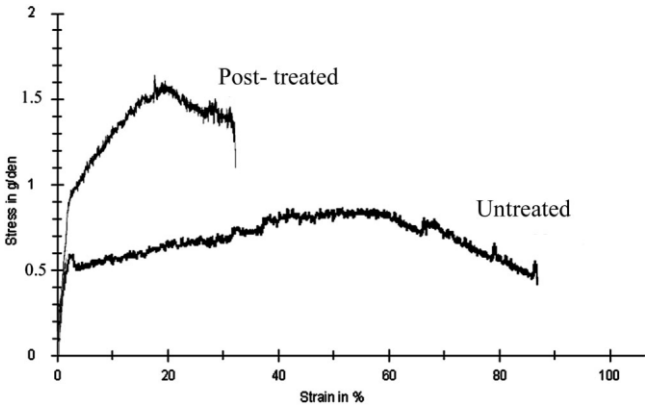

Figure 9 Stress–strain curve of the bundles of untreated and posttreated uniaxially aligned PAN nanofibers.

TABLE III
Mechanical Properties of the Bundles

Sample	E-Modulus (MPa)	Strain at *F* max (%)	Stress at *F* max (MPa)
Untreated	2786 ± 200	43.34 ± 5	99 ± 12
Posttreated	4575 ± 220	18.37 ± 3.5	178 ± 15

crystalline order and mechanical properties of these treated samples are not high enough and prohibit the application of these nanofibers in many fields. Further work studying the effects of posttreatments (e.g., stretching of bundles of electrospun uniaxially aligned PAN nanofiber in hot water and steam) on the mechanical properties, crystallinity and molecular orientation are currently ongoing.

CONCLUSIONS

1. Uniaxially aligned PAN nanofibers were electrospun using a collector consisting of two pieces of electrically conductive substrates separated by a gap. Our study showed that the density of aligned nanofibers was decreased by increasing the width of the gap. But the degree of alignment of nanofibers and proportion of aligned nanofibers mass to the all increased at first by increasing these parameters and then decreased. The electrospinning conditions (i.e., the tip to target distance, voltage and width of the gap) that gave the best alignment of fibers for 10–15 wt % PAN/DMF concentrations were experimentally obtained.
2. The X-ray diffraction results of PAN nanofibers showed that the crystallization was retarded during electrospinning, but no change in lattice spacing was observed. The posttreatments permitted some additional development of crystalline order and the CI% increased up to 17.4%.
3. The bundle became much stronger but relatively with lower elongation after the post-treatments. The values of E-Modulus and tensile strength at break were 4575 and 178 MPa (1.62 g/den) respectively, for posttreated bundle.

The authors gratefully acknowledge the assistance of Mr. Azarnasab and Ms. Esrafilzadeh. Mr. Rezai is acknowledged for preparing the SEM images.

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