Alignment and Optimization of Nylon 6 Nanofibers by Electrospinning

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ABSTRACT: Nonwoven electrospun nylon 6 nanofibers produced with formic acid under different concentrations have been examined. The effects of the solution properties, electric field, and spinneret-to-collection distance on the fiber uniformity, morphology, and average diameter have been established. The optimum polymer solution concentration (20 wt %), applied voltage (15 kV), and spinning distance (8 cm) have been found to make uniform nylon 6 fibers. A simple technique that can produce a bundle of aligned electrospun fibers suspended between two grounded disks is described. Alignment and stretching of the fibers are derived by the electrostatic interactions between the positive electrode on the spinneret and the grounded disks. The gap between the disks and the collection time have been varied to systematically study the degree of alignment and the density of the collected nylon 6 fibers. The number of the distributed fibers in the bundle can be controlled by the alteration of the deposition time, the voltage, and the width of the gap. Scanning electron microscopy images have indicated a greater degree of fiber alignment with increasing disk gaps and collection times. The article also provides a comprehensive review of the design of various mechanisms for nanofiber alignment. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3023–3032, 2008

Key words: fibers; nylon; nanotechnology

INTRODUCTION

Fiber diameters in the nanorange have great advantages in volume-to-space and strength-to-weight ratios. Although conventional textile fibers have a fiber diameter ranging from 1 to 50 μm,[1] electrospinning is one of those technologies that enable the production of continuous nanofibers of the order of 10^{-9} m from polymer solutions or melts in high electric fields.[2–6] Electrospinning is a fiber-spinning technique that relies on electrostatic forces to produce fibers in the micrometer to nanometer range.[7,8] Under the influence of an electrostatic field, a pendant droplet of the polymer solution or melt at the spinneret is deformed into a conical shape (Taylor cone). If the voltage surpasses a threshold value at which electrostatic forces overcome the surface tension, a fine charged jet is ejected. As these electric static forces increase, the jet will elongate and accelerate by the electric forces. The jet undergoes a variety of instabilities, dries, and deposits on a substrate as a random nanofiber mat. A typical polymer is dissolved in a solvent or combination of solvents with a viscosity ranging from 1 to 200 P.[9] Although nanofibers of more than 30 different types of organic polymers have been successfully produced by electrospinning, a systematic study of the optimization of nylon 6 for fiber alignment is yet to be achieved.

It has been found that the morphology, such as the fiber diameter, and uniformity of electrospun polymer fibers are dependent on many processing parameters, including the hydrostatic pressure in the spinneret, external electric field, polymer concentration, molecular weight of the polymer, viscosity, conductivity, dielectric permeability, surface tension, distance from the spinneret to the collector, volume feed rate, and ambient conditions. The polymer jet trajectory has a very complicated three-dimensional whipping form caused by bending instability. As a result, most nanofibers obtained so far are in a nonwoven form, which can be useful for limited applications such as filtration,[10–13] tissue scaffolds,[14] implant coating films,[15] and wound dressings.[16] However, when continuous single nanofibers or uniaxial fiber bundles are obtained, full advantage of nanofabrication may be realized. To that effect, alignment of the nanofibers during formation is extremely important and is the focus of this work.

Consequently, the effects of the solution properties and processing parameters on the morphology of electrospun nylon 6 nanofibers have been systematically studied to produce a wide range of fiber diameters with a uniform fiber diameter distribution. A useful review is also presented on the design of various mechanisms for nanofiber alignment, followed by an effective method of generation of a bundle of

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aligned three-dimensional nanofibers over a large area by the introduction of a gap between two known surfaces.

EXPERIMENTAL

Materials and electrospinning process

Nylon 6 and formic acid were purchased from Sigma–Aldrich (Gillingham, United Kingdom). The polymer solution was fed from a 5-mL capacity syringe (Fisher Co., Leicestershire, United Kingdom) to a vertically orientated (25-gauge) blunt-ended metal needle via Teflon tubing. The flow rate was digitally controlled with a positive displacement syringe pump (M22 PHD 2000, Harvard Apparatus) (Edenbridge Kent, United Kingdom). The needle was connected to one electrode of a high-voltage direct-current power supply (MK35P2.0-22, Glassman, New Jersey, USA).

Process parameters

Various polymer solution concentrations ranging from 15 to 25 wt % were prepared by the dissolution of the polymer in formic acid. Fibers were obtained with an earthed collection system, which consisted of a copper collector plate measuring 15 cm × 15 cm. Typical operating regimes were flow rates of 0.2 mL/h, applied voltages between 12 and 18 kV, and a working distance of 5–11 cm. A schematic of the experimental setup used in these experiments is shown in Figure 1. For aligning the fibers, two copper circular disks (30 mm o.d., 2 mm thick) were used as collection disks. They were positioned with grounded alligator clips, with the top of the disks being 8 cm from the needle. Investigations of the effect of the gap width and collection time on the degree of alignment and the density of fibers were carried out. The applied voltage was fixed at 15 kV, the polymer solution concentration was 20 wt %, and the gap width was set at 2, 3, 4, 5, and 6 cm at 15-, 30-, 60-, and 120-s collection times.

Scanning electron microscopy (SEM)

The samples produced for both aligned and random nanofibers were collected on aluminum stubs. For aligned nanofibers, the aluminum stubs with parallel strips of super-glue tapes were passed through the suspended fibers between the collection disks. These samples were sputter-coated with gold–palladium for 45 s at 18 mA. Fibers were examined with a Hitachi S-530 scanning electron microscope (Berkshire, United Kingdom) at an accelerating voltage of 10 kV. Micrographs were taken at three random areas of each sample between 20,000 and 40,000× magnifications. These results were used to compile fiber diameter distribution profiles.

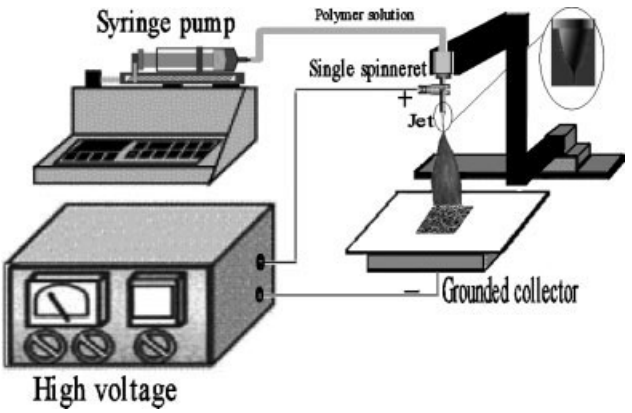

Figure 1 Schematic illustration of the setup for electrospinning.

RESULTS AND DISCUSSION

Morphology of electrospun nonwoven fiber mats

Figures 2–4 show a series of SEM images of the micromorphology of the nanofibers obtained from the electrospinning of nylon solutions with three different concentrations. At a 15% concentration, fibers less than 200 nm in diameter are formed, with some beads being formed (drops of polymer over the nonwoven mat). These beads disappear as the fiber diameter is increased with increasing polymer concentration. Different fiber morphologies occur at different concentrations and have a significant effect on the surface area to the volume ratio of the fiber. Electrospinning using a concentrated nylon solution produces smooth, free nanofibers with thicker fiber diameters. A nylon concentration of 20% or more by weight results in ribbonlike nanofibers (see Fig. 2). The formation of ribbonlike nanofibers is due to rapid solvent vaporization from the surface of the jet and has previously been described.[17]

Effect of the polymer concentration on the fiber morphology

As the electrospinning results show in Figure 5, the diameter of the electrospun fibers dramatically decreases with decreasing polymer concentration. When the spinning distance is small and the polymer solution has a low concentration (15%), the solution reaches the collection plate before full evaporation of the solvent. This explains the formation of droplets and beads at the low polymer concentration and short spinning distance. Fewer beads were observed in electrospun fibers at a higher concentration. The changing of the fiber morphology can probably be attributed to a competition between the surface tension and viscosity. Reneker et al.[18] sys-

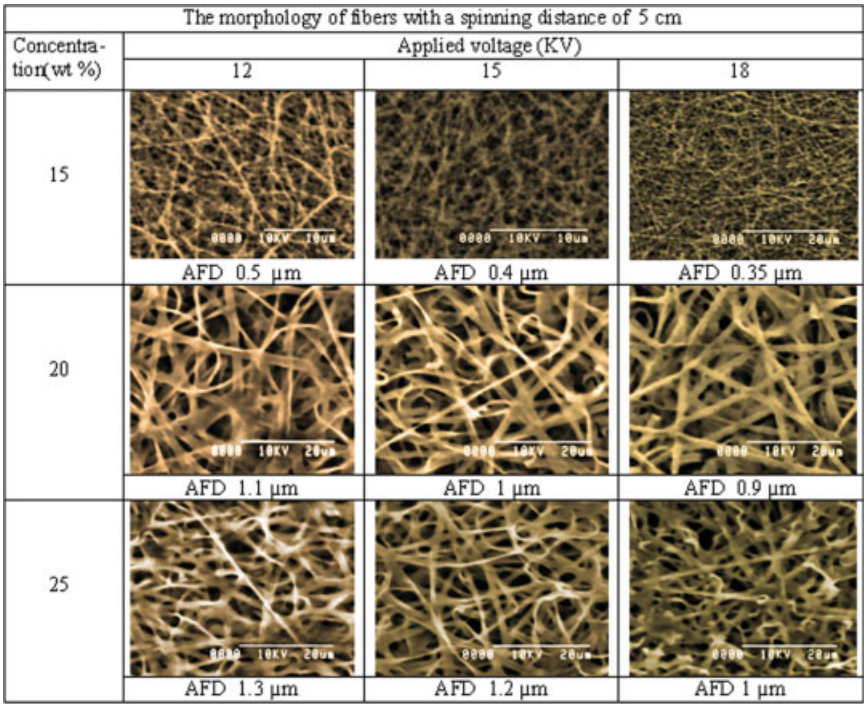

Figure 2 Average fiber diameter (AFD) at electric fields of 12, 15, and 18 kV and polymer solution concentrations between 15 and 25% with a constant spinning distance of 5 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tematically investigated the influence of solution properties of poly(ethylene oxide) on the density of beads contained in the electrospun fibers. It has been found that the viscosity and surface tension are the most important factors that affect the morphology of the resultant fibers.[19] Vancso et al.[20] indi-

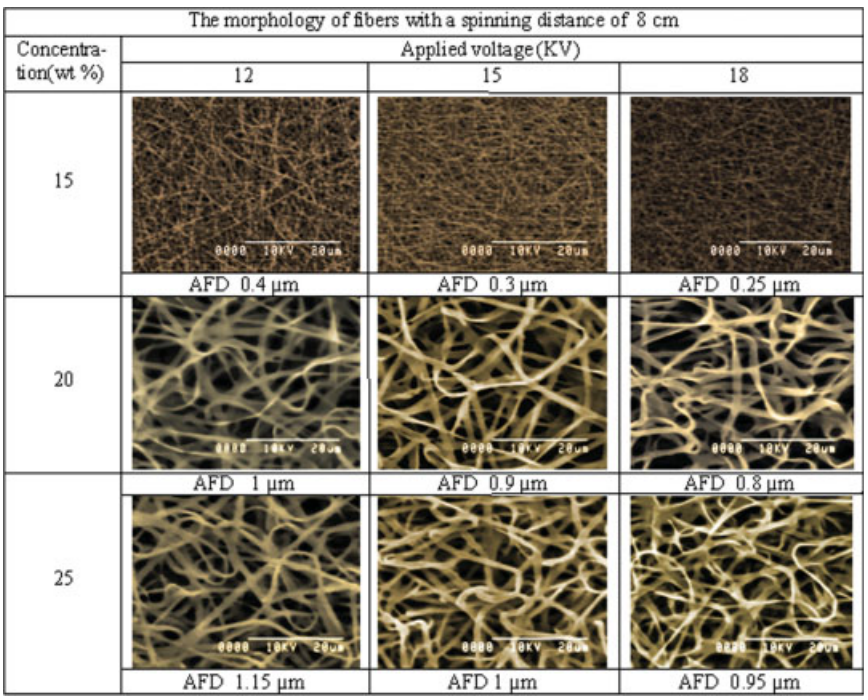

Figure 3 Average fiber diameter (AFD) at electric fields of 12, 15, and 18 kV and polymer solution concentrations between 15 and 25% with a constant spinning distance of 8 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

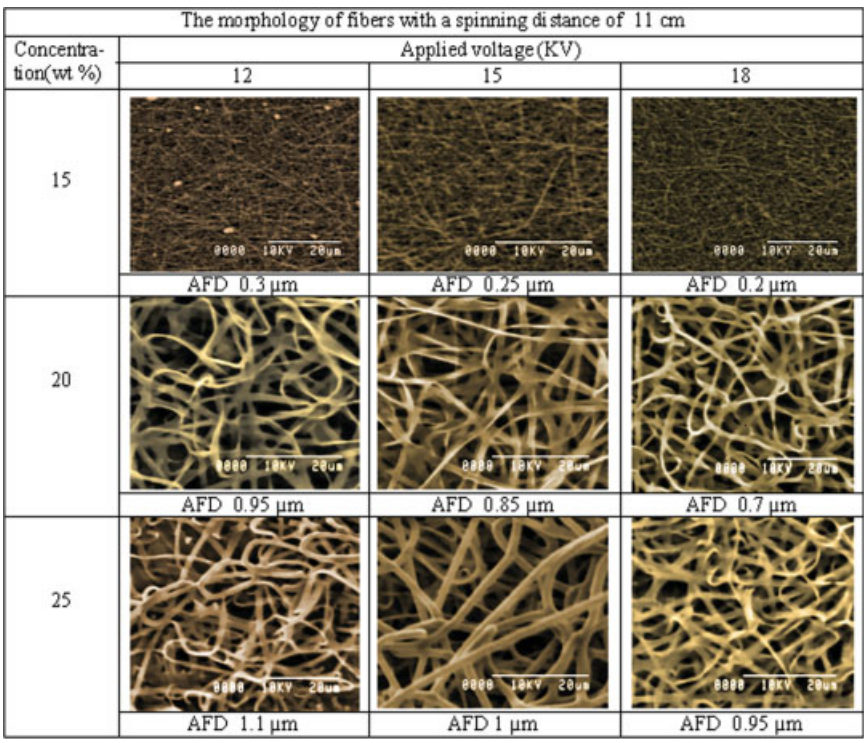

Figure 4 Average fiber diameter (AFD) at electric fields of 12, 15, and 18 kV and polymer solution concentrations between 15 and 25% with a constant spinning distance of 11 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cated that viscoelastic forces prevented the formation of beads and allowed the formation of smooth fibers.

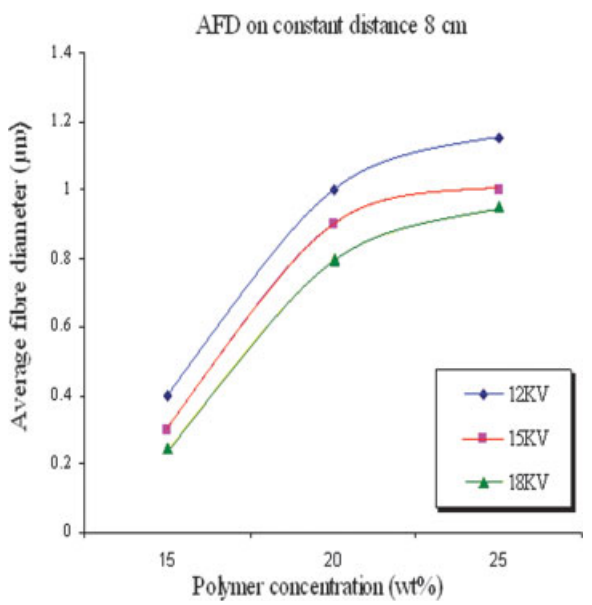

Figure 5 Relationship between the average fiber diameter (AFD) and solution concentration at three electric fields with a constant spinning distance of 8 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of the voltage and spinning distance on the fiber morphology

We optimized the process parameters by studying the influence of the electric field and spinning distance on the fiber morphology. Figure 6 shows the relationship between the mean fiber diameter and electric field with a constant concentration of 20 wt %. Figure 7 shows the relationship between the average fiber diameter and spinning distance with an applied voltage of 15 kV. The fiber diameter is not changed dramatically with various applied voltages. Comparing the fiber diameters at 5-and 8-cm spinning distances with the same electric field and concentration (see Fig. 6) shows that fiber diameters obtained at a 8-cm spinning distance are lower than those obtained at a 5-cm spinning distance in the concentration range of 15–25%. For a 20% nylon concentration, an increase in the electric field from 15 to 18 kV leads to a decrease in the average fiber diameter from 850 to 800 nm and from 850 to 750 nm under 8- and 11-cm spinning distances, respectively. One might suggest that this result is due to the longer spinning distance, which enables the solvent to evaporate more efficiently even at the same electric field strength, thus leading to a smaller fiber diameter in comparison with the fiber diameter obtained at a 5-cm spinning distance.

The applied voltage may affect some factors such as the mass of polymer fed from the tip of the pend-

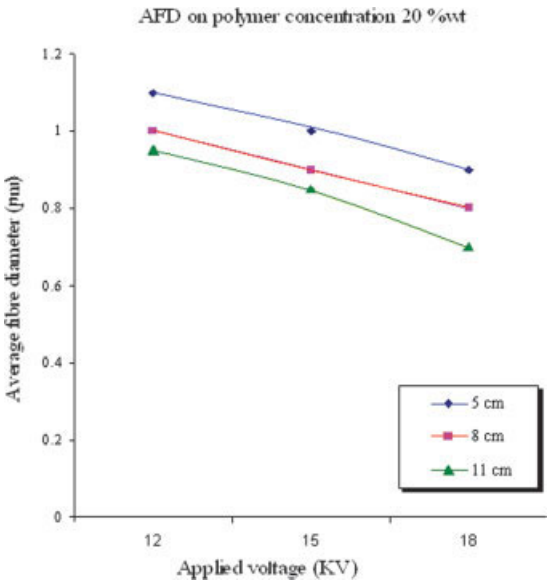

Figure 6 Relationship between the average fiber diameter (AFD) and applied voltage with a solution concentration of 20% at spinning distances of 5, 8, and 11 cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

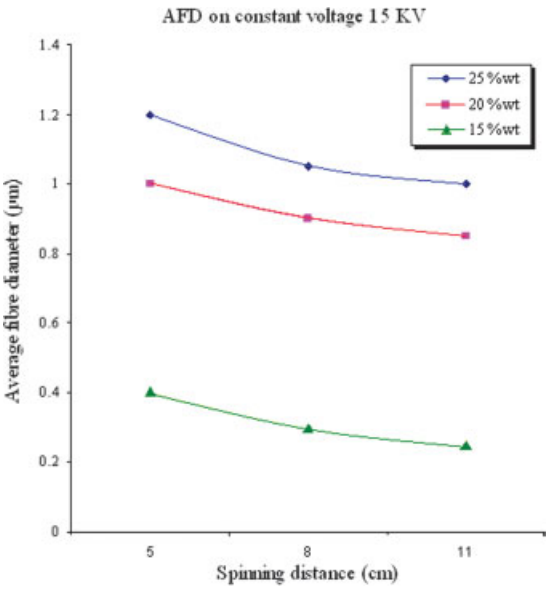

Figure 7 Relationship between the average fiber diameter (AFD) and spinning distance with an applied voltage of 15 kV at polymer solution concentrations of 15, 20, and 25 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ant, the elongation level of a jet by an electrical force, and the morphology of the jet (single or multiple jets).[21] A balance among these factors may determine the final diameter of the electrospun fibers. Increasing the applied voltage does increase the electrostatic force and create smaller diameter fibers, but it also draws more solution out of the spinneret. If the increasing electrostatic force draws much more solution out of the needle, the fiber diameter will increase with increasing applied voltage, as reported by Demir et al.[22] In general, increasing the applied voltage to a certain level changes the shape of the pendant drop from which the jet originates, so a stable shape cannot be achieved. As a result, the stability of the liquid jet is weakened, and this might lead to an increase in the density of beads in the electrospun fibers.

Process optimization

Processing parameters need be optimized to electrospin nylon 6 into nanofibers with the desired morphology. The applied voltage reflects on the force to pull a solution out from the spinneret, so a higher applied voltage causes higher solution consumption.

On the other hand, the applied voltage affects the charge density and thus the electrical force, which influences the elongation of the jet during electrospinning. Briefly, electrospun nanofibers with a smaller diameter can be produced with a lower polymer solution concentration, but nonuniform/beaded fibers are found if these parameters were either too high or too low. These results are in agreement with published reports for polymers other than nylon 6.[23–26] The analyzed SEM image shown in Figure 8 indicates that the optimal conditions for producing a uniform fiber diameter distribution are a polymer solution concentration of 20 wt %, an applied voltage of 15 kV, and a spinning distance of 8 cm. These parameters were made constant for producing uniform nylon 6 fibers, which assisted the subsequent investigation of the alignment of nylon 6 nanofibers.

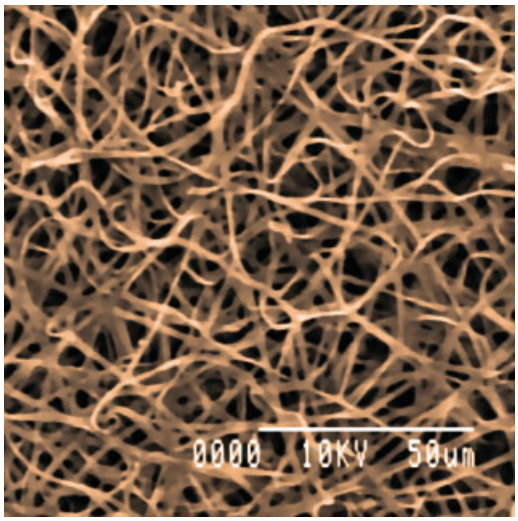

Figure 8 SEM image of 20% nylon 6/formic acid nanofibers at a voltage of 15 kV and a distance of 8 cm with a uniform fiber diameter distribution of 900 ± 50 nm.

Concept of alignment and review of nanofiber alignment methods

The alignment of fibers is important for engineering the nanostructure but most important for enabling the twisting of aligned fiber bundles for the development of nanoyarns, which are the focus of this work. In recent years, researchers have explored novel mechanical and electrostatic methods to control the electrospinning process, thus moving away from collecting random and disordered nanofibers to collecting ordered aligned nanofibers. The results are promising, but further improvement is needed for effective fiber alignment. It has been suggested that by the rotation of a cylinder collector at a very high speed, up to thousands of revolutions per minute, electrospun nanofibers could be oriented circumferentially.[27–31] If the surface speed of the cylinder is slower than the stretching speed, randomly deposited fibers can be collected. If the rotating speed is too high, continuous fibers cannot be collected because the fiber jet will break; even so, the degree of alignment that could be achieved with this method is limited only to a partial alignment and still needs improvement. Another simple method of obtaining a tubular structure with well-aligned electrospun nanofibers in a circumferential direction and at an angle to the longitudinal axis of a tube has been proposed.[32,33] It states that some control of the direction of the alignment of the electrospun nanofibers is exercised and it is possible to develop a tube made of nanofibers with great versatility in its mechanical strength. In a U.S. patent,[34] it is reported that by the asymmetric placement of a rotating and charged mandrel between two charged plates, electrospun ultrafine fibers can be oriented circumferentially to the longitudinal axis of the tubular structure. In both techniques, small-diameter fibers remain randomly oriented.

Zussman et al.[35] and Inai and coworkers[36,37] modified the design of a drum and used a tapered, wheel-like disk as the collector. The tiplike edge substantially improves the concentration of the electrical field by attracting almost all nanofibers. The charged fibers are continuously wound on the edge when the disk is rotating at a relatively high speed. Provided that a nanofiber is attached to the wheel tip, it exerts a repulsive force on the next fiber attracted to the tip. This repulsion results in a separation between the deposited nanofibers. They have further reported on a technique for a hierarchical assembly of nanofibers into crossbar nanostructures.[38] The collector disk is equipped with a table that collects the nanofibers and can be rotated about the z axis. In this technique, the area in which the fibers are deposited is limited and needs further investigation. In another effort for obtaining aligned fiber patterns,[39] a sharp needle was used as a counter electrode placed in an insulating, rotating cylinder. This method allows a tube made of circumferentially aligned fibers to be obtained. As the layer of fibers increases, however, the counter electrode does not hold a significant draw on the fibers. As a result, the thickness of the aligned fibers obtained is restricted.

Another approach to fiber alignment was recently developed by Haung et al.[40] by simply placing a rectangular frame structure under the spinning jet. Further work was done by the rotation of a multiframe structure on which electrospun poly(ethylene oxide) nanofibers could be continuously deposited. Xia et al.[41,42] and Dalton et al.[43] recently demonstrated the importance of the geometrical configuration of a conductive collector on the alignment of electrospun nanofibers. A simple and versatile method that generates uniaxially aligned nanofibers over large areas by introducing a gap into a charged collector has been presented. By the alteration of the configuration of electrostatic forces acting on the fibers spanning across the gap, nanofibers were stretched across the gap to form a parallel array. The effects of the gap width and applied voltage on the degree of fiber alignment were investigated by Morshed et al.[44] They experimentally studied the electrospinning conditions (i.e., the tip-to-target distance, voltage, and gap width) that produce the best alignment of fibers for 10–15 wt % polyacrylonitrile/dimethylformamide concentrations. It has been reported that 11 kV provides the highest alignment of nanofibers with a fixed corresponding concentration of 15 wt % and gap width of 3 cm. In another report, a simple and successful method for spinning sheets of 1-cm-wide strips of aligned nanofibers was presented by Chase et al.[45] In this technique, copper wires spaced evenly in the form of a circular drum as a collector of nanofibers have been used. A further investigation in this work is needed on the effects of the rotation speed, gap distance between the wires, wire diameter, and polymer type. Bhattarai et al.[46] produced highly aligned fibers of controllable size by winding a copper wire as an electrode on an insulating cylinder. Although highly aligned fibers can be obtained, the deposited fibers on the wire are more difficult to extract.

A newly developed scanned electrospinning technique that enables the rapid fabrication of aligned polymeric nanowires was described by Kameoka et al.[47] Although it presents new opportunities for the manufacture and applications of nanowire devices, the electrospinning process conditions (spinning distance and vaporization of the solvent) should be established. By modifying the target electrodes, Kim and Kim[48] presented a simple method to fabricate aligned poly(ε-carprolactone) fibers. Suspended aligned nanofibers were generated on a dielectric substrate by the control of the electrostatic field

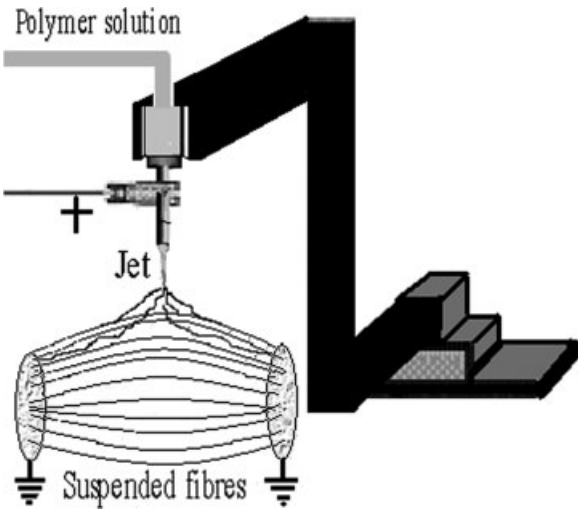

Figure 9 Experimental setup for electrospinning three-dimensional aligned nanofiber bundles.

between the target electrodes, which were subjected to an applied alternating-current field. The alignment of nanofibers was dependent on the applied frequency, field strength, and shape of the target electrode. A novel technique of manufacturing aligned electrospun fibers by the use of two oppositely placed metallic needles connected to positive and negative voltage was presented by Li et al.[49]

In this technique, fibers coming out of the two needles combine into a yarn, and this yarn is wound onto a cylinder collector rotating at a high speed. Fibers manufactured by this technique are continuous but are curly at a low take-up speed and tightly clustered at a low concentration.

In conclusion, with an understanding of the electrospinning jet behavior under the influence of an electric field, it is possible to deposit fibers at fixed points. Having established the optimum nylon 6 spinning conditions, we further present a modified technique, derived from refs. 41–43, that is based on a three-dimensional alignment principle shown in Figure 9.

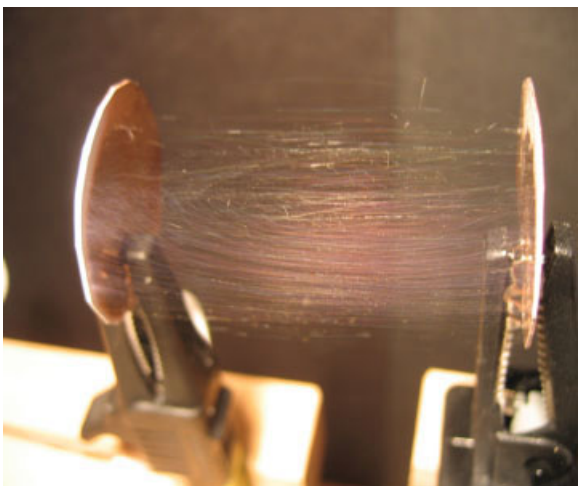

Figure 10 Photograph of an array of aligned (20% nylon 6/formic acid) nanofibers, 5 cm in length, deposited between two changed disks after 120 s with an applied voltage of 15 kV and a spinning distance of 8 cm. The obtained fiber diameter was 800 ± 40 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

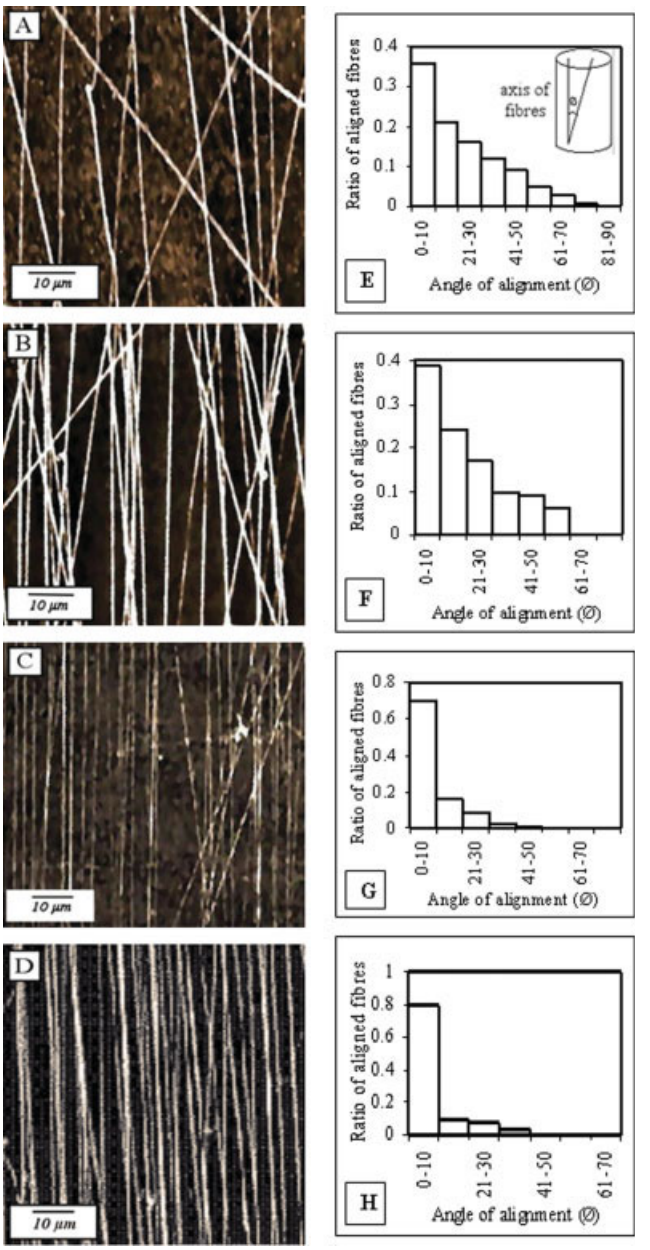

Figure 11 (A–D) SEM images of aligned nylon 6 nanofibers collected under a 4-cm gap distance at 15, 30, 60, and 120 s, respectively, and (E–H) charts of the ratio of aligned nanofibers per angle of alignment related to the SEM images. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

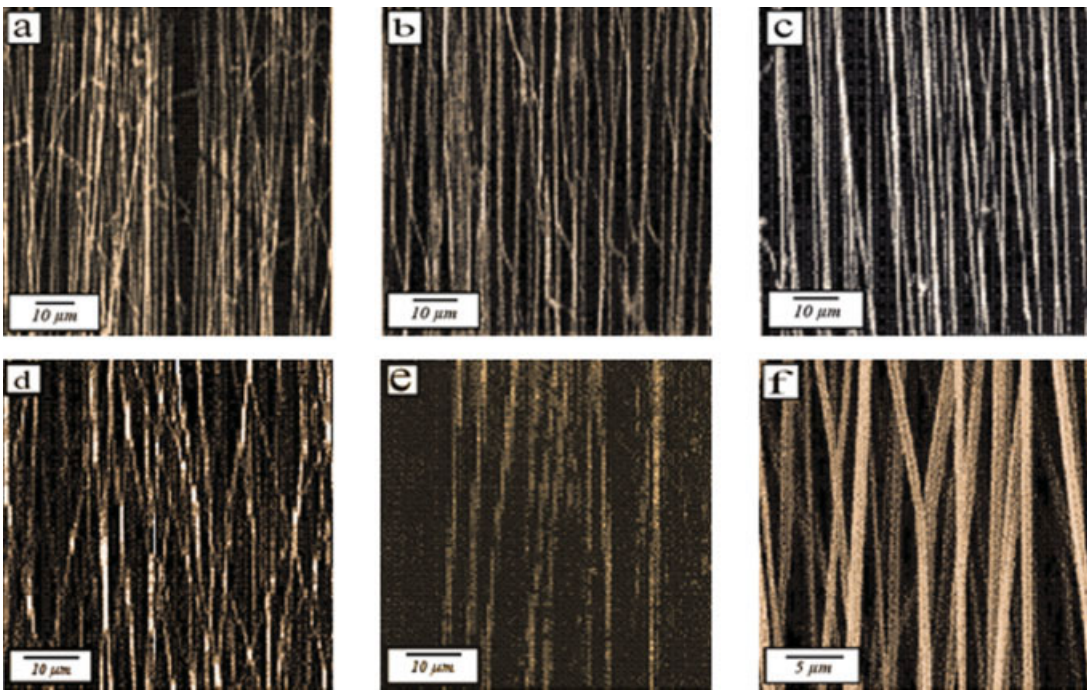

Figure 12 SEM images of aligned nylon 6 nanofibers with a constant collection time of 120 s and gap spaces between the disks of (a) 2, (b) 3, (c) 4, (d) 5, and (e) 6 cm. (f) SEM image of approximately uniform fibers 800 ± 40 nm in diameter with a 5-cm gap space and 120-s collection time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Alignment of electrospun nanofibers

Unlike electrospun fibers directly deposited onto a grounded collector as a random mesh, centimeter-long fiber bundles were deposited in a curved parallel path between two copper disks in seconds, as shown in Figure 9. After 15 s of spinning, parallel aligned nanofibers between the two disks were observed. The magnified micrograph in Figure 10 shows that the aligned nanofibers are perpendicular to the axis of the collection disks and have a uniform diameter distribution. Alignment and stretching of the fibers are derived by electrostatic interactions between the positive electrode on the spinneret and the grounded disks. As a result, the polymer fiber travels toward the disk collector, one end of the fiber is attached to one of the disks, and the other end of the fiber is pulled toward the other disk. Once the charged fibers have moved into the gap between the disks, the fibers will induce opposite charges on the surface of the disks. These opposite charges will attract the fibers to the grounded disks, leading to the alignment of the fibers in the gap between the circular disks. The SEM images in Figure 11 show that well-aligned fibers have been formed, having diameters in the range of 800 ± 40 nm over four different collection times. The aligned fibers collected have lower average fiber diameters because their relaxation and expansion values are lower than in the case of random collection, leading to a decrease in the fiber diameters.

Effect of the collection time and space distance on the degree of alignment

The degree of parallelism of the aligned fibers was measured by image analysis. Our experiments indicated that the collection time had a major effect on the alignment-parallelism degree of the fibers. Figure 11(A) shows that the fibers are not well aligned along the axis of the fiber bundle, whereas perfectly parallel nanofibers can be seen in Figure 11(D). This means that the degree of fiber alignment increases with the collection time. On the other hand, because of the electrostatic repulsion force increasing between the deposited fibers with time, a long collection time will lead to worse alignment. Figure 12 shows SEM images of electrospun nanofibers after 120 s of spinning, with the gap (space) distance between the disks ranging between 2 and 6 cm. These images indicate a greater degree of alignment with the increase in disk space and the significant effect of the collection time.

Parameters affecting the density of deposited fibers

The experiment carried out shows that the number of nanofibers distributed in the bundle depends on

parameters such as the collection time and the gap width. However, the applied voltage, spinning distance, and flow rate are the main effects on the mass of the deposited fibers and the number of branches generated from the electrospinning jet. With an increase in the applied voltage for a given spinning distance, nanofiber branching will increase, resulting in difficulties for aligning nylon 6 nanofibers. On the other hand, with an increase in the voltage, the drawing forces will increase, improving the alignment across the gap. The images in Figures 11 and 12 show that as the deposition time is increased and the width of the gap is decreased, the number of nylon 6 fibers increases, and this makes the bundle denser. In fact, this can be explained by the theory of mass conservation.

The results obtained by Morshed et al.[44] showed a low relative proportion of aligned polyacrylonitrile nanofiber mass for all electrospun polyacrylonitrile nanofibers (ca. 10–20%) with changes of the gap width. These results are expected because the conductive metallic collector surfaces are small; the metallic collector will not have a significant drawing on the fibers as the layer of fibers increases. In our method, a higher proportion of aligned nanofiber mass has been obtained because of the large effective face surfaces of the disks, which stretch and span the fibers across the gap of the disks.

It has been noted that at a gap distance of 10 cm, few nylon 6 fibers were collected across the gap of the collection disks. When the collection disks were separated by a distance larger than 10 cm, the electrospinning jet had difficulty in depositing the nylon 6 fibers across the gap of the collection disks. In conclusion, the optimum disk distance for spinning nylon 6 nanofibers is 4–5 cm. This provides the basis for twisting the fiber bundle for the formation of uniform nanoyarns.

CONCLUSIONS

In this study, the electrospinning of nylon 6 nanofibers has been achieved. The effects of solution properties and process parameters on the morphological appearance and average fiber diameter have been investigated, and the process has been optimized. It has been noted that the polymer solution concentration plays an important role in determining the fiber morphology. A simple method that generates a bundle of aligned three-dimensional nylon 6 nanofibers by introducing a gap between two charged copper disks has been described and discussed. Our experiments demonstrate that the number of the distributed fibers in the bundle can be controlled by the alteration of the applied voltage, deposition time, and gap width of the disks. SEM images have indicated a greater degree of alignment as the space between the disks and collection time increase. Our analysis has shown that the electrostatic repulsion forces between the deposited fibers also have a significant effect on the degree of alignment. The maximum length of the fiber bundle collected was 10 cm, depending on the collection geometry and processing parameters. The strength of the forces exerted on the nanofibers is related to the applied voltage, collection time, and gap width.

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