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Continuous Electrospinning of Aligned Polymer Nanofibers onto a Wire Drum Collector

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ABSTRACT

The process of electrospinning produces polymeric fibers with diameters ranging from the micrometer to the nanometer scale. As the fibers are produced, they are usually spun and collected in a random mat lacking structural orientation. In some applications there is interest in parallel alignment of nanofibers to produce structures with unique electrical, optical, and mechanical properties. A simple and successful method for spinning sheets with one centimeter wide strips of aligned nanofibers is presented. The technique uses copper wires spaced evenly in the form of a circular drum as a collector of the electrospun nanofibers. Aligned nanofiber sheets can be collected easily without disturbing the aligned structure, and the method is robust.

Electrospinning was first explored in the 1930s[1] as a simple and versatile method for making fibers from polymer solutions with diameters typically ranging from 50 to 500 nanometers. Current interests in nanostructured materials have stimulated renewed efforts in electrospinning. Electrospun nanofibers have large surface-to-volume ratios compared to conventional textile fibers. The large surface areas enhance properties such as adsorption of chemicals. Mat structures made of electrospun nanofibers have small pore openings which make them suitable for military and civilian filtration applications.[2] Aligned nanofibers in particular have potential applications in composite materials, reinforcements, electrochemical sensing, bone and blood vessel engineering and tissue engineering, which often require well-aligned and highly ordered architectures.[3−7]

Common methods of polymer fiber production include melt spinning, solution spinning, and gel state spinning.[8,9] These methods rely on mechanical forces to produce fibers by extruding a polymer melt or solution through a spinneret and subsequently drawing the resulting filaments as they solidify or coagulate. By using these methods, typical fiber diameters in the range of 5 to 500 microns can be produced. The minimum fiber diameter is on the order of a micron, and the lengths of the fibers vary from centimeters (in laboratory production) to kilometers (in commercial production). Electrospinning provides a straightforward way of producing long polymer fibers with diameters as small as 10 nm and up to a few microns in diameter. The length of the nanofibers depends on the time of electrospinning and can be thousands of kilometers in a short period of time. Under normal conditions, bending instabilities present in the polymer jet stream cause randomly oriented fibers with various diameters and structures during the electrospinning process.[10,11] However, disordered structures are problematic for use in device fabrication in such areas as microelectronics and photonics.[12]

Several approaches have been considered for the alignment of polymeric nanofibers. Researchers have explored novel methods including mechanical and electrostatic ways to align continuous polymer and ceramic nanofibers. Dersch et al. demonstrated the orientation of polyamide nanofibers on a metal frame as the collector. The observed orientation is believed to be due to the polymer jet jumping back and forth from one side of the frame to the other, apparently because of electrostatic charging effects.[13] Zussman et al. attained alignment in small regions by the use of a sharp needle to position and align individual polymer nanofibers into parallel arrays.[14,15] Most recently, Sundaray et al. have shown that as-spun fibers could be aligned (parallel and cross patterns) when an insulated cylinder attached to the axle of a DC motor is used as the substrate. In that case the substrate was rotated with a high speed of approximately 2000 rpm.[16] Xia et al. have fabricated polymeric and ceramic nanofibers as axially aligned arrays by the use of a collector consisting of two pieces of electrically conductive substrate separated by a gap whose width could be varied from micrometers to several centimeters.[17]

In our approach the grounded platform for collecting the nanofibers is a copper wire-framed drum. The drum has two

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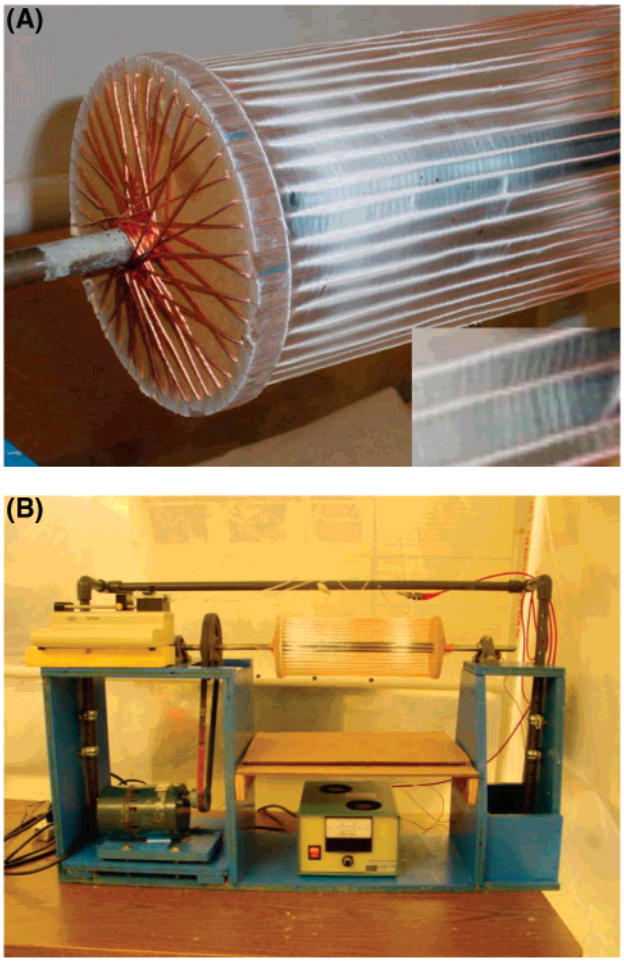

Figure 1. (A) Plexiglas disk with copper wires. Electrospun nylon nanofibers are collected on the copper wires. The nanofiber mat shows stratified layering in the magnified image. (B) Apparatus for rotating the copper wire drum during electrospinning.

circular nonconducting Plexiglas disks 12.7 cm in diameter with a 1.2 cm diameter hole cut in the center. Each disk has 6 mm deep saw cut notches placed one centimeter apart around the circumference. The two disks are mounted on a rod and spaced 30 cm apart with PVC pipe. The copper wire is stretched between the slots cut into the edges of the disks shown in Figure 1. The copper wire is grounded.

A solution of 20 wt. % nylon-6 and formic acid was prepared by dissolving 20 g of nylon-6 beads (Aldrich, CAS 25038-54-4) in 80 g of formic acid (Fisher Scientific CAS 64-18-6). The ingredients were mixed and set aside for 24 h at room temperature to obtain uniform dissolution of the polymer into the solvent. The polymer solution was collected into a 5 mL capacity syringe (Becton Dickinson, Franklin Lakes, NJ) for electrospinning.

The polymer solution was forced through a stainless steel needle using a syringe pump at a constant rate of 1.5 μL/min. The needle of the syringe was held at 20 kV relative to ground using a high voltage power supply (Gamma High Voltage Research, model D-ES30PN/M692). The drum was located fifteen centimeters below the needle. The copper wire drum was connected to a motor with two pulleys and rotated at a speed of 1 rpm. The electrospinning voltage was gradually increased to 20 kV until the solution started spinning across the copper wires. Individual nanofibers cannot be seen with the naked eye, but after 5 min of spinning, a nanofiber sheet oriented perpendicular to the symmetry axis of the wire drum was observable.

Many of the nanofibers collect directly on the copper wire closest to the needle. As the drum slowly rotates, the next copper wire attracts the nanofibers and the nanofibers stretch perpendicular to the copper wires to span the gap between the wires. The rotation rate of the drum was held constant in the experiments reported here (1 rpm) but should be explored in future work. The rotation rate is likely to affect the mass ratio of nanofibers lying on the copper wires to the mass of nanofibers spanning the gap between the copper wires. Slower rotation rates are expected to result in more mass of nanofibers on the copper wires and faster rotation rates result in more mass of nanofibers spanning the gap between the wires.

Alignment of the nanofibers is driven by electrostatic interactions allowing the charged nanofibers to stretch and span across the gap between the wires and to form axially aligned arrays over large areas. Xia et al. studied the forces acting on the surface of fibers during alignment.[17] The charged nanofiber experiences two sets of electrostatic forces: the first set originates from the applied electric field and the second one between an incoming section of charged fiber and charges on the surfaces of fibers attached to the wires. The first electrostatic force is in the same direction as the applied electric field, hence the nanofibers move to the vicinity of the copper wires. Because of the rotation of the drum a given wire is closest to the needle for a short period of time. As the rotation continues the next wire rotates closer to the needle. The electrospinning fibers follow the electric field attraction of the next wire and thus the fibers move from one wire to the next. Due to the second set of electrostatic forces the fibers stretch across the shortest distance in the gap between the wires and thus cause the fibers to align.

A sample of aligned fibers was collected on carbon tape (Nissin EM. CO. LTD) and analyzed with a scanning electron microscope (SEM, JEOL JSM 5310) to confirm alignment. Typically, carbon tape is placed on a grounded surface and samples are collected during the electrospinning process. That approach is not practical with the rotating drum. For this work the carbon tape was dabbed gently on the drum containing nanofibers at various time intervals. The fibers adhered to the tape and the tape was placed on stubs used for SEM. The samples were sputter coated with gold for 2 min to reduce charging effects.

Electrospun nylon-6 samples were analyzed at various time increments in the electrospinning process ranging from 5 min to 2.5 h. Samples were not taken earlier than 5 min due to the inability to see such small quantities of nanofibers with the human eye. Figure 2 shows several SEM images of various samples taken from the wire drum. Several sets of experiments were conducted and images taken to confirm alignment. Images were taken at various magnifications to acquire different perspectives.

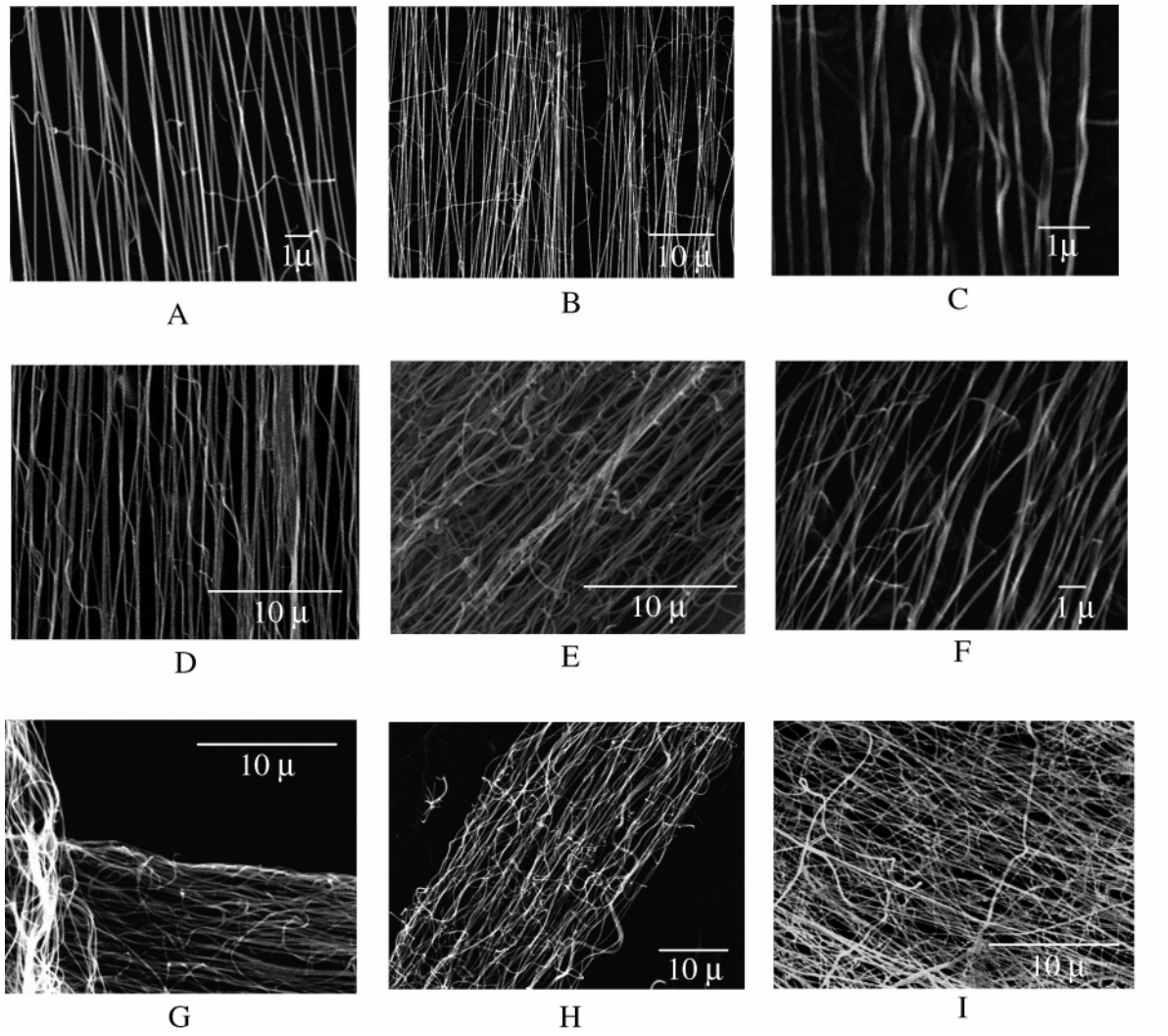

Figure 2. SEM images of axially aligned polymer nanofibers on conductive copper wire drum: (A, B, and C) alignment after 5 min of spinning time. (D, E) after 15 min, (F, G, and H) after 40 min, and (I) after 2.5 h of spinning time.

As seen in the SEM images, good alignment is present up to approximately 15 min of electrospinning. After 15 min, the mat of fibers begins to thicken and entanglements form. However, decent alignment is still present up to 40 min, as seen in Figure 2G−H. For longer periods of time, the fibers spin in random patterns and alignment is gradually lost as the thickness of the fiber mat increases, as seen in Figure 2I after 2.5 h of electrospinning. Figure 2A−C shows excellent alignment is observed after only five minutes of electrospinning. Figure 2G shows an example of how the fibers can entangle or be disturbed if not carefully collected, vastly changing the properties of the aligned fibers.

The loss in alignment with thicker mats is not yet understood. It is possibly due to an accumulation of charge in the fiber mat, but the jet was not observed to stray away from the grounded wires as is often the case with low conductivity polymers. It is also possible that the nylon mat acts as a conductor. In this latter case the thickened mat on the wire drum fills in the gaps between the wires with a grounded surface and the electrospinning jet effectively experiences the grounded field of a solid drum surface instead of the field produced by the array of copper wires.

Aligned mats that are thick enough to cut and handle are formed in about 15 min of spinning. The mats increase in thickness and durability with time. Because the nanofibers are suspended over the gaps between the wires, they can easily be transferred onto other surfaces for subsequent treatments such SEM imaging as well as mechanical and optical property testing. SEM images of the samples taken from the copper wire rotating drum apparatus yielded consistent alignment surpassing any of the other alignment methods we have tested to form mats of aligned fibers. Future research will investigate the effects of rotation rate, gap distance between the wires, wire diameter, and polymer type.

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