Fabrication of Continuous Aligned Polyvinylpyrrolidone Fibers via Electrospinning by Elimination of the Jet Bending Instability

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Received 14 September 2009; accepted 8 December 2009
DOI 10.1002/app.31938
Published online 22 February 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, we successfully fabricated highly aligned polyvinylpyrrolidone (PVP) fibers and crossed mats by restraining and eliminating the jet bending instability through a dual-opposite-spinnerets electrospinning (DOSES) method. The DOSES process was photographed by a digital camera, and the morphology of the fibers was analyzed with field emission scanning electron microscopy. We argue that the elimination of the jet whipping and bending instability was achieved by adjusting the concentration of the polymer solution. When the concentration of PVP solution was raised to more than 15 wt %, two individual fibers stuck together were obtained without the appearance of the jet bending instability at a suitable take-up velocity. This study demonstrated solid improvement in both the alignment of the polymer yarns and the fabrication of individual fibers side by side. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3676–3681, 2010

Key words: fibers; nanotechnology; viscosity

INTRODUCTION

The electrospinning technique has been widely investigated in the past decade as a low-cost and convenient method to produce microfibers and nanofibers for various applications.[1–4] Generally, electrospun fibers are deposited randomly on a flat collector in the form of nonwoven mats. However, the inability of fibers to align and arrange limits the applications of electrospun fibers and mats.[5] So it is of significance to control the orientation of fibers, and many methods have been developed to solve this problem.[6] The fibers can be guided to assemble along a certain direction when the flat collectors are changed to some specific structure. For instance, some researchers have introduced a rotating drum to replace the collecting plate and achieved good fiber alignment.[7–10] A rotating wheel with a sharp edge has also been used as the collector to obtain highly aligned fibers.[11–13] The sharp edge can restrict the flight path of the jet and limit the laid position of fibers on the surface of the sharp edge to produce highly aligned individual fibers. Also, a gap method with two spaced parallel electrodes has been successfully applied to the generation of highly aligned fibers.[14–16] Sometimes, the distribution of the electric field has been changed, and the spread of jet whipping might have been restrained when specific auxiliary electrodes were added to the collectors. Some groups have introduced bias and focusing electrodes to conventional electrospinning devices to manipulate the electric field.[17–19] The depositing area of fiber mats was greatly suppressed, and an ordered arrangement of fibers was gained. Teo, Wu, and coworkers[20–22] demonstrated that the electric field could be focused and excellent alignment of fibers could be produced by the positioning of knife-edged blades under the collector. In addition, Carnell et al.[23] used an auxiliary electrode to eliminate the jet whipping and bending instability associated with the electrospinning process. Well-aligned fibers were obtained by this method, and crossed mats with multilayers were fabricated on the basis of fibers aligned in a single direction. A gas jacket was also used to weaken the widely observed bending instability. Zhou et al.[24] used gas flow to assist the alignment of electrospun fibers and obtained well-aligned polymeric nanofibers covering a larger area with a

Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2006AA02Z4E9.
Contract grant sponsor: National Key Technology Research and Development Program of China; contract grant number: 2006BAI03A18.

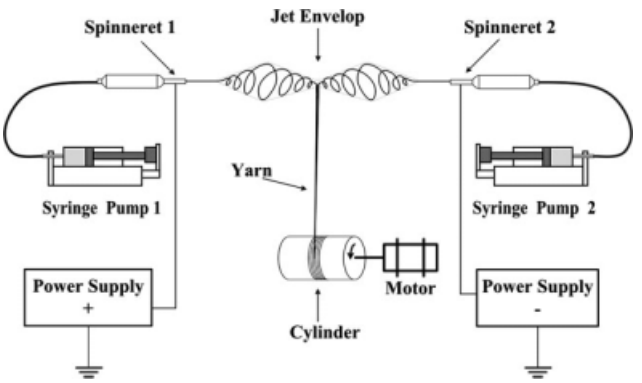

Figure 1 Schematic illustration of the DOSES setup.

length of more than 20 cm. Also, Sarkar et al.[25] reported a "biased AC electrospinning" method to restrict the bending instability and achieved highly aligned fibers and crossed mats.

We revealed a dual-opposite-spinnerets electrospinning (DOSES) method with which large numbers of uniaxially well-aligned fibers with diameters of submicrometers were fabricated.[26] It proved to be an effective way to restrict the chaotic path of the electrospinning jets and eliminate the residual charge accumulation on the fibers. However, the jet bending instability still existed in the collecting process and made this process unstable and easily interrupted. However, in this article, we report that the concentration of the polymer solution could be adjusted to restrict and eventually eliminate the jet bending instability and well-aligned electrospun fibers could be more steadily fabricated through an improved DOSES method.

EXPERIMENTAL

Materials

Polyvinylpyrrolidone (PVP; weight-average molecular weight = 130,000, Beijing Organic Chemical Plant, Beijing, China) was chosen for the experiment and used without further purification. In a typical procedure, PVP was dissolved in ethanol and stirred by a magnetic stirrer for about 2 h. Different concentrations of PVP/ethanol solutions (10, 12, 15, 18, and 20 wt %) were prepared.

Setup and electrospinning

The schematic setup for the DOSES method is shown in Figure 1. Two flat-tipped stainless steel spinnerets (inner diameter = 0.7 mm) were assembled in opposite directions with an interval of 15 cm. The polymer solution was pumped to the spinnerets with a dual-syringe infusion pump (TS2-60, Longer Precision Pump Co., Baoding, China) and connected to the spinnerets. Two spinnerets were connected to the opposite electrical potentials provided by high-voltage power supplies (DW-103-1AC, Tianjing Dongwen High Voltage Power Supply Plant, China). A rotating cylinder 10 cm in diameter was placed under the spinnerets as a collector, and a Teflon slice was pasted on the surface of the cylinder to gather fibers. The vertical distance between the spinnerets and the cylinder was 15 cm. The flow rate of solution was 14 μL/min, and the applied voltage of the opposite power supplies were ±4000 V.

Measurement and characterization

The conductivity of the PVP solutions was measured by a conductivity meter (DDS-307, Precision & Scientific Instrument Co., Ltd., Shanghai, China), whereas the viscosity was gauged by a rotary viscometer (DV-1, Xuchang Science Apparatus Co., Shanghai, China). A video contact angle system (OCA-20, DataPhysics, Germany) was used to measure the surface tension of the PVP solutions. The visualization of the DOSES process was obtained by digital photography (EOS-1D Mark II, Canon). These captured images allowed us to observe the jet path and fiber-generation process from the spinneret arrangement to the point of collection. Polymer fibers were attached to the surface of Teflon slices and coated with platinum with a JEOL (Tokyo, Japan) JFC-1200 coater. Then samples were photographed with a field emission scanning electron microscope (JSM-6700F) with an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

When the voltages were applied to the two spinnerets supplied with PVP solutions, jets were ejected from the two spinnerets. At a lower concentration (e.g., the 10% PVP solution), the jets underwent a helical whipping process and attracted each other, so two spindly envelopes were formed because of the interaction of whipping and attractive electric forces. The two envelopes collided near the middle point of the two spinnerets and stuck to each other randomly, so a cluster of fibers was generated, and the fibers were drawn from the random cluster to generate well-aligned arrays. A photograph of this process is shown in Figure 2(a). Because the collision of fibers was random and unstable, the rupture of fibers, which led to the discontinuity of the collecting process, occurred easily in the collecting process. The restoration of this process introduced unordered fibers and affected the fiber alignment. So the generated fibers could not withstand a very high take-up velocity. The maximum steady take-up velocity for the 10% PVP solution was 4.25 m/s, which did not match the velocity of the jet path, so some curly fibers were occasionally included in the aligned

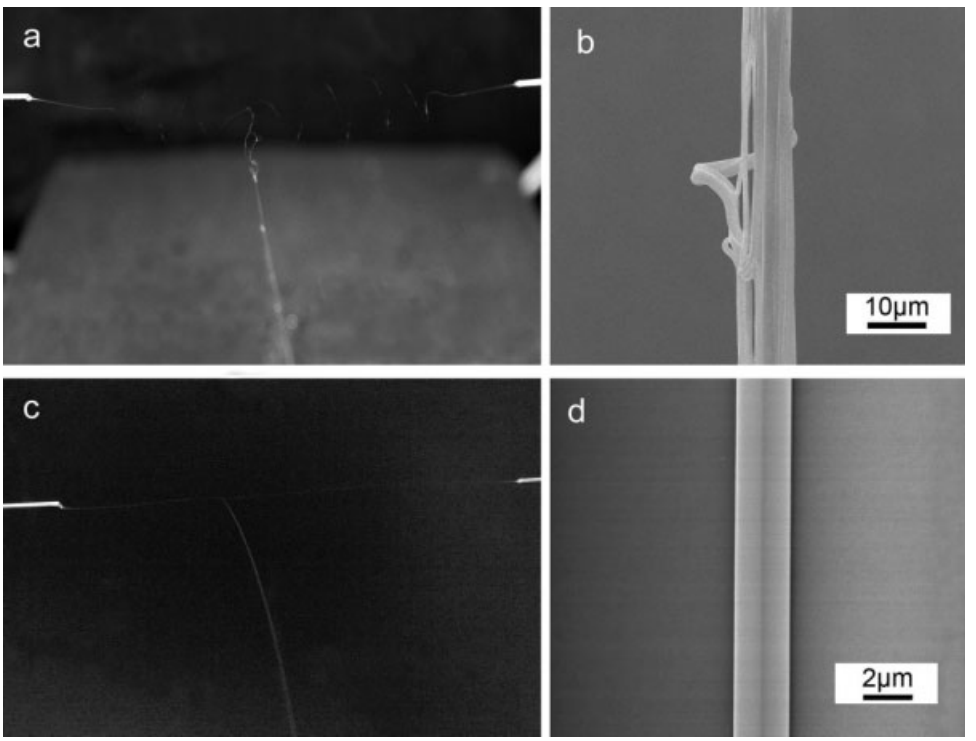

Figure 2 (a) Digital image of helical jets with bending instability, (b) an individual yarn with some curly fibers from a 10% PVP solution that was collected for a round at a surface velocity of 4.25 m/s, (c) digital image of two straight jets stuck together to form a single fiber, and (d) a yarn of two individual fibers from a 15% PVP solution that was collected for a round at a surface velocity of 10.62 m/s. [The videos of the two processes are shown in the supporting information (Appendices A and B).]

yarn. Figure 2(b) shows an individual yarn with some curly fibers from the 10% PVP solution, which was collected for a round at a surface velocity of 4.25 m/s. However, the bending instability of the jet was weakened with increasing PVP concentration. When the concentration increased to 15% and the yarns were collected at a take-up velocity of 10.62 m/s, the bending process disappeared. A photograph of the DOSES process without bending instability is shown in Figure 2(c). In this case, two straight individual fibers collided with each other to form a single yarn. The yarns were drawn to the rotating cylinder and arrayed ideally on the surface of the cylinder. Figure 2(d) reveals the scanning electron microscopy (SEM) image of the generated yarn consisting of two individual fibers.

These results show that the PVP concentration was a significant factor affecting the bending instability in the course of DOSES. To further understand the influence of the concentration on the jet bending instability and the fiber alignment, 10, 12, 15, 18, and 20% PVP/ethanol solutions were prepared and electrospun at different take-up velocities. Figure 3 shows the SEM images of the generated PVP fibers with different concentrations. At low concentrations (10 and 12%), as shown in Figure 3(a,b), most fibers were arrayed in an orderly manner in the same direction, but there were also a few skew and curly fibers. The imperfection in the alignment of fibers was mainly caused by the existence of the jet bending instability and the velocity mismatch. When the concentration was higher than 15%, the jet bending process disappeared at a proper take-up velocity, and ideal alignment without any unorderly fibers was achieved. Figure 3(c–e) shows the SEM images of the fibers generated from the 15, 18, and 20% PVP solutions. The fibers arrayed mostly in the same direction, and no curly fibers were discovered. A crossed array was also generated by the electrospinning of multiple layers in a 0/90° arrangement similar to the structures produced by Carnell et al.[23] and Zussman et al.[27] This was achieved by the following steps: (1) we electrospun the first layer onto a Teflon slice attached to the cylinder, (2) then, we took off the Teflon slice and rotated it for 90° and reattached it to the cylinder, and (3) finally, we electrospun the second layer on top of the first. Fibers were collected for 1 min in each direction. A high degree of alignment was also observed in this configuration, which is shown in Figure 3(f).

The average diameters of the fibers were measured with ImageJ software (NIH, Bethesda, MD) and are shown in Figure 4(a). This figure reveals that the average diameters continuously increased from 970 ± 92 to 3020 ± 412 nm with increasing solution concentration. Figure 4(b) shows the matching

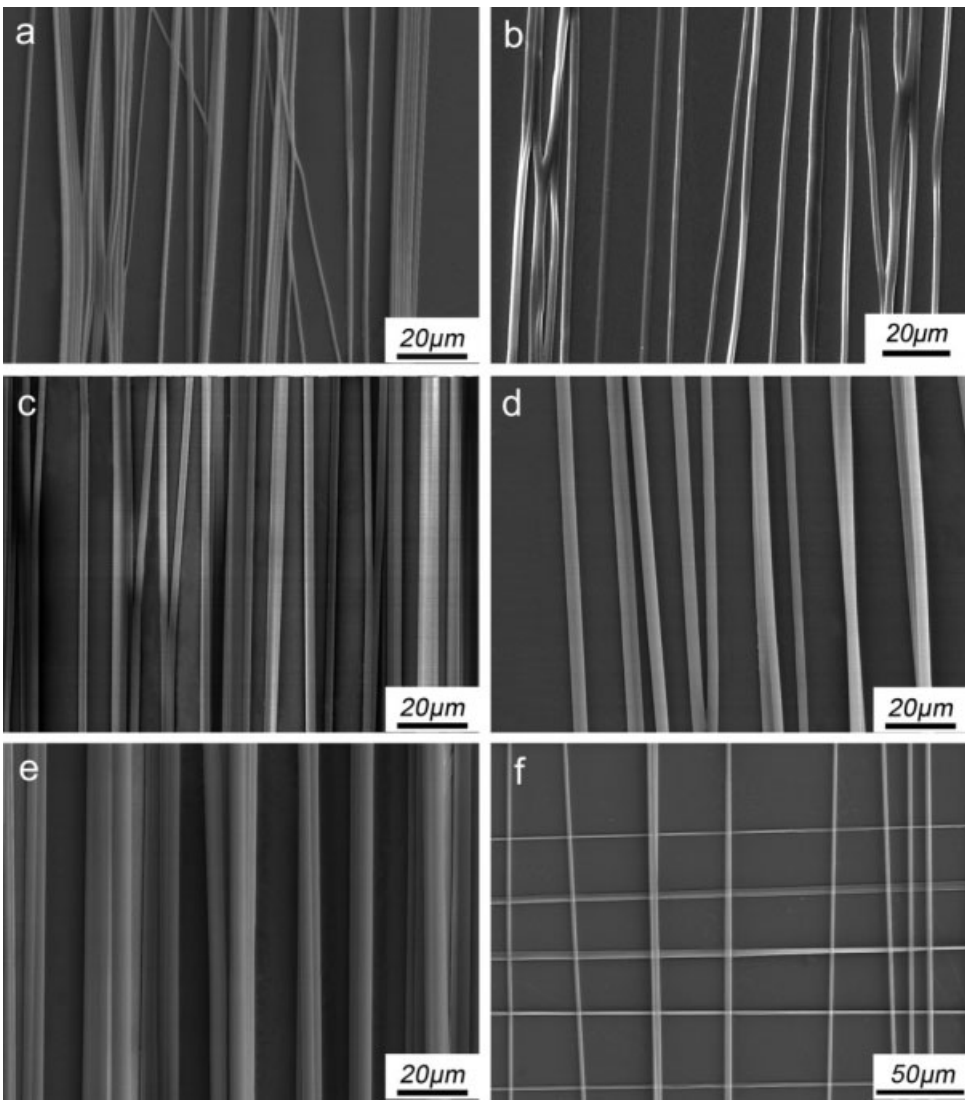

Figure 3 SEM images of aligned and crossed PVP fibers from solutions with different concentrations, (a) 10, (b) 12, (c) 15, (d) 18, (e) and 20%, and (f) SEM image of a crossed array with a 0/90° arrangement.

take-up velocity as dependent on the solution concentration. At a low concentration, the jet traveled with a helical path because of the bending instability, so the jet velocity was very high because of the whipping process, and the collision process caused the fibers to overlap with one another and form a yarn with several individual fibers. However, the yarn did not undergo a very high velocity that matched the jet velocity because the collision was random and the strength of fibers was not high enough. The fiber diameter increased with increasing concentration of solution; simultaneously, the yarn could bear a higher take-up velocity without rupture. So the maximal take-up velocity increased with the concentration of solution, and the effect of alignment also got better because of the more sufficient stretching of fibers along with the increase of take-up velocity. The limits of the steady take-up velocities for the 10 and 12% solutions were 4.25 and 5.66 m/s, respectively. When the limits were exceeded, the collecting process was easily interrupted, and the alignment got worse. When the concentration was higher than 15%, the fibers were strong enough to bear the stretching, and the take-up velocity could match the jet velocity, so the bending instability could be eliminated, and the jets would travel in a straight line to form an individual fiber. In this experiment, the fibers were collected at 10.62 m/s without bending instability for the 15% solution, at 7.08 m/s for the 18% solution, and at 5.66 m/s for the 20% solution. At this time, the suitable take-up velocity merely depended on the jet path velocity, which decreased along with increasing concentration.[28] As the cylinder was continuously accelerated, the generated fibers were thinned and crooked to the direction of cylinder. So the optimum take-up velocity also decreased with increasing solution concentration, and alignment without any disarrayed fibers was achieved when the two velocities matched.

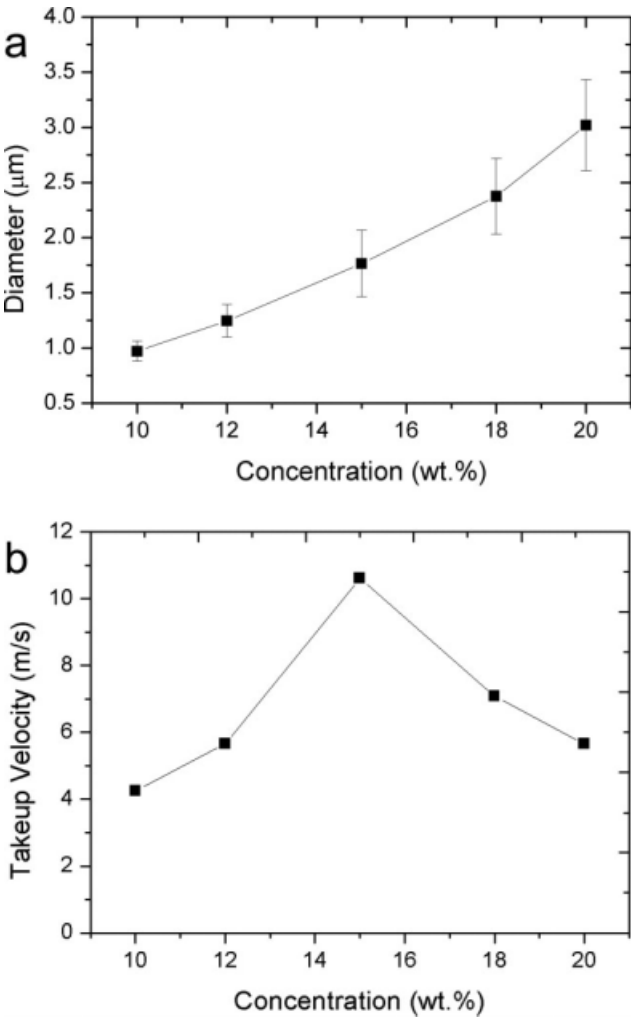

Figure 4 (a) Average diameters of the fibers and (b) matching take-up velocities dependent on the concentrations of the PVP solutions.

In the DOSES process, when electrically charged jets were ejected from the spinnerets, they initially moved along the external electric field between the two spinnerets and finally collided near the middle point of two spinnerets. The terminals of the jets were fixed by the opposite jets, so the bending behavior was restricted, and the shape of the envelopes varied from conical to spindly. According to the model proposed by Renker et al.,[29] when a jet was perturbed away from the axis of traveling path, it was forced by the external electric field force, viscoelastic force, surface tension force, and repulsive Coulombic force. The repulsive Coulombic force pushed the jet away from the straight line and made the perturbation larger; however, the resultant force of viscoelastic force and surface tension force counteracted the bending instability.[29,30] The Coulombic force was mainly determined by the operating parameters and the conductivity, whereas the internal force was chiefly influenced by the viscosity and the surface tension.[31,32] The properties of the PVP solutions used in this experiment are summarized in Table I. The solution conductivities were almost the same (ca. 24S/cm), whereas the surface tensions varied from 26.47 to 29.35 mN/m when the concentration increased from 10 to 20%. On the other hand, the viscosity increased more than 24 times from 0.192 to 5.081 Pa s. So only the viscoelastic force changed markedly along with increasing solution concentration. At a low concentration, the viscoelastic force and surface tension force were easily overcome by the repulsive Coulombic force; this resulted in the growth of the jet bending. Along with the increase of the solution concentration, the viscoelastic force increased to a value that was large enough to counteract the repulsive Coulombic force. So the perturbation could not grow large, and the jets would travel always in a straight line when the fibers were collected under a suitable velocity. Therefore, in addition to the fixation of the terminal of the jets, viscosity was a key factor in the elimination of bending instability.

CONCLUSIONS

With the DOSES method, we proved that the elimination of jet whipping and bending instability could be achieved by adjustment of the concentration of the polymer solution. When the concentration of the PVP solution increased to more than 15% and the take-up velocity matched the jet path velocity, two straight jets without bending instability stuck together in the middle of the two spinnerets and formed an individual well-aligned yarn. Ideally

TABLE I
Conductivity, Viscosity, and Surface Tension of PVP Solutions with Different Concentrations

Concentration (wt %)	Conductivity (S/cm)	Viscosity (Pa s)	Surface tension (mN/m)
10	23.2	0.192	26.47
12	24.1	0.679	26.97
15	24.2	1.811	28.38
18	24.5	3.837	29.01
20	24.6	5.081	29.35

aligned electrospun PVP fibers and crossed mats were produced with this method. The mechanism of how the solution concentration affected the bending instability was also discussed qualitatively. This study demonstrated a solid improvement of both the alignment of polymer yarns and the fabrication of individual electrospun fibers.

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