Needleless Electrospinning of Nanofibers With a Conical Wire Coil

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In this article, we have demonstrated a novel needleless electrospinning of PVA nanofibers by using a conical metal wire-coil as spinneret. Multiple polymer jets were observed to generate on the coil surface. Up to 70 kV electric voltage can be applied to this needleless electrospinning nozzle without causing 'corona discharge.' Compared with conventional needle electrospinning, this needleless electrospinning system produced finer nanofibers on a much larger scale, and the fiber processing ability showed a much greater dependence on the applied voltage. Finite element calculation indicates that the electric field intensity profiles for the two systems are also quite different. This novel concept of using wire coil as the electrospinning nozzle will contribute to the further development of new large-scale needleless electrospinning system for nanofiber production. POLYM. ENG. SCI., 49:1582–1586, 2009. © 2009 Society of Plastics Engineers

INTRODUCTION

The conventional electrospinning setup uses a hollow needle as the spinning nozzle [1, 2]. Each nozzle only generates one polymer jet that results in very limited fiber productivity, up to 300 mg per hour per needle. The small needle diameter also results in highly concentrated electric field near the nozzle surface, making it easy induce "corona discharge" under a high applied voltage, which is the main reason for the stoppage of electrospinning process. The maximum applied voltage for a needle electrospinning setup is normally <30 kV and is also highly humidity dependent [3]. The low operating voltage also leads to coarse nanofibers.

Much attention has been paid to the development of large-scale electrospinning techniques. The strategy of improving the nanofiber production is mainly based on increasing the number of needle nozzles [4–6]. However, the multineedle spinneret needs a large operating space and careful design of the relative spacing between the needles so that strong charge-repulsion between the jets and adjacent needles and the associated uneven fiber deposition can be avoided. In addition, using gas jacket was reported to enhance the processing ability of single needle nozzle [7]. The gas jacket, however, influences the nanofiber morphology and fineness.

Recently, needleless electrospinning setups have been developed [8–11]. Without using a needle nozzle, a number of jets could be generated even from a widely open liquid surface. The pioneering work was reported by Yarin and Zussman [9], who used a magnetic fluid to agitate the uppermost polymer solution in order to initiate the concurrent production of multiple jets from a flat polymer solution surface. Later on, Jirsak et al. [10] described the generation of multiple jets from a liquid uploaded on a slowly rotating horizontal cylinder, which was subsequently commercialized by Elmarco under the brand name of Nanospider^{TM}. In addition, Dosunmu et al. [11] reported the formation of multiple jets using tubular plastic foam spinneret.

The generation of multiple jets from needleless electrospinning has been explained as the waves of an electrically conductive liquid self-organize in mesoscopic scale and finally form jets when the applied eclectic field intensity is above a critical value [8]. Therefore, the formation of jets and resultant fiber morphology in needleless electrospinning will be highly influenced by the electric field intensity around the spinneret and the electric field intensity profile in the electrospinning zone. However, it has not been established if a needleless electrospinning setup can produce not only larger fiber quantity but also finer nanofibers than the needle-based electrospinning system.

In this article, we reported a needleless electrospinning setup using a cone-shaped metal wire coil as spinneret. Using polyvinyl alcohol (PVA) as model polymer, we have demonstrated that a large number of jets can be generated simultaneously on the conical coil surface, which results in improved fiber productivity. Furthermore, the resultant nanofibers had a finer average fiber diameter than that produced by a typical needle electrospinning system.

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EXPERIMENTAL

Materials and Measurements

PVA (average molecular weight: 146,000–186,000; 96% hydrolyzed) was obtained from Aldrich-Sigma and used as received. PVA solutions (with different wt%) were prepared by dissolving the PVA powder in deionized water at 90°C, with intensive stirring for about 12 h and without adding any additives in the solution. The fiber morphology was observed under a scanning electron microscope (SEM; Leica S440). The average fiber diameter was calculated from the SEM photos with the aid of an image analysis software (Image*Pro*+4.5).

Needleless Electrospinning Setup

The apparatus for the conical wire-coil needleless electrospinning is depicted in Fig. 1a. It comprised a cone-shaped nozzle made from copper wire coil (wire diameter: 1 mm), with a cone angle of about 120° and a gap between the adjacent wires of 1 mm. The height of the cone was 15 mm. The wire was connected to a high-voltage power supply (ES100P; Gamma High Voltage Research) via the base side. A metal mesh was used to collect the nanofibers.

RESULTS AND DISCUSSION

Two reasons led us to use a conical wire coil, rather than a flat open surface, as spinneret. First, from geometry and fluidics, a conical wire coil is an open container which can hold more viscous fluid in it, compared with a flat open surface. As a result of a slightly higher liquid pressure formed by the loaded fluid, the viscous fluid is

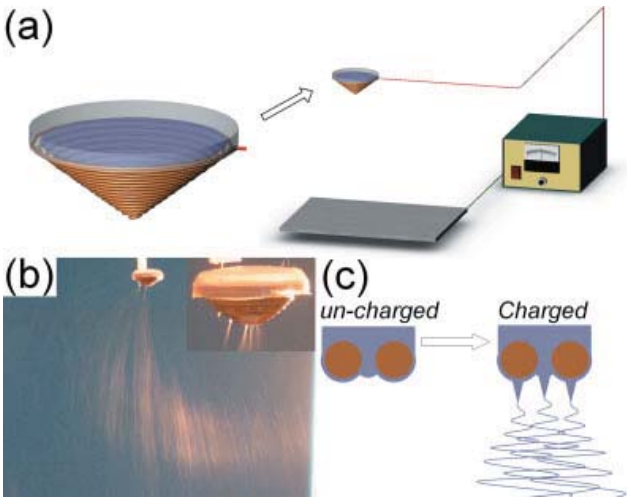

FIG. 1. (a) Schematics of wire coil electrospinning setup. (b) Photograph of the electrospinning process (inset: multiple jets). (c) Illustration of jet formation on the coil surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

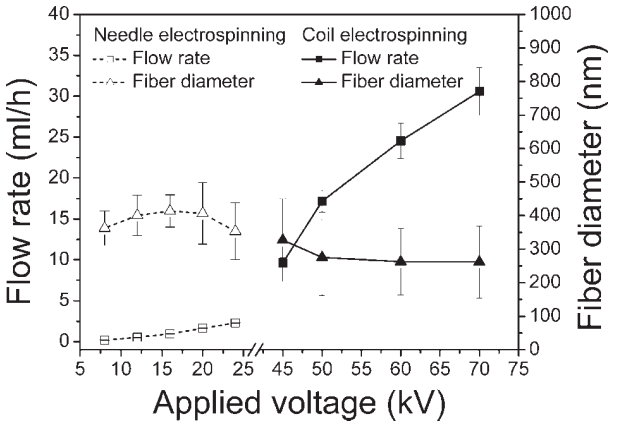

FIG. 2. Dependence of volume rate and average fiber diameter on applied voltages. PVA concentration = 9 wt%; collecting distance = 15 cm.

easier to cover evenly underside the surface of the cone. Second, a higher electric potential is normally formed on the outer surface of the cone. This enables the electrospinning of nanofibers only from outer cone surface to the collector.

In electrospinning, when a viscous PVA solution was filled into the wire cone, it was retained by the conical coil without leaking out because of the surface tension and the viscoelastic nature of the polymer solution. When a high electric voltage was applied to the wire coil, the charged polymer solution moved down and covered the outer surface of the wire. A number of jets were then generated mainly on the conical wire surface (Fig. 1b and c). It was also found that the jets were generated from the areas that had sufficient polymer solution on the surface. Once the solution was exhausted temporarily in one area, the jet formation stopped, but restarted in other areas with replenished polymer solution.

Figure 2 shows the volume rate of PVA solution being processed under different applied voltages for both the conical wire coil and a needle electrospinning system. For the wire coil system, the minimum voltage to generate jets was 45 kV, and the lowest voltage that led to the occurrence of corona discharge was 70 kV. Between the two voltage values, nanofibers could be electrospun without any difficulty. With the increase in the applied voltage, the volume rate increased swiftly from 9.6 to 30.6 ml/h, and no liquid drops were observed to form from the nozzle.

The typical nanofiber morphology is shown in Fig. 3. The nanofibers electrospun from 9 wt% PVA solution at different applied voltages showed bead-free fibrous morphology. The variation in applied voltage led to changes in the fiber fineness. With the increase in the applied voltage from 45 to 50 kV, the average fiber diameter decreased from 327 ± 123 to 275 ± 113 nm (see Fig. 2). Furthermore, increasing the voltage resulted in minute change in the fiber diameter and distribution. The fiber productivity for this electrospinning system can be estimated based on the volume rate. According to the volume

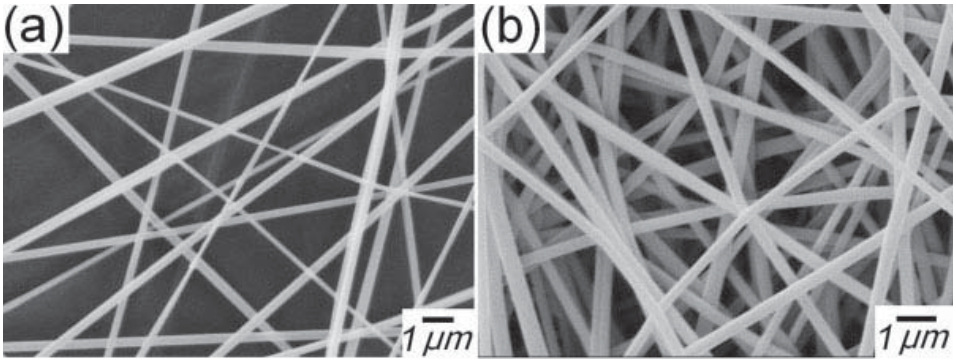

FIG. 3. SEM images of typical nanofibers electrospun from (a) conical wire-coil electrospinning ($V = 60$ kV), and (b) conventional needle electrospinning ($V = 22$ kV). PVA concentration = 9 wt%; collecting distance = 15 cm.

rate data given in Fig. 2, the highest production rate for producing dry nanofibers was found to be 0.86 and 2.75 g/h at 45 and 70 kV, respectively.

For comparison, a needle-based electrospinning setup (21-gauge needle: outer diameter, 0.82 mm; inner diameter, 0.51 mm) [12] was also used to electrospin nanofibers using the same polymer solution. The lowest voltages for initiating polymer jet and occurrence of "Corona discharge" in the needle electrospinning were 8 and 25 kV, respectively. The range of operating voltage (8–24 kV) used for this electrospinning system was similar to many other needle electrospinning processes. The fibers electrospun within this voltage range showed good fiber uniformity. A critical volume rate, i.e., the maximum flow rate of polymer solution not generating liquid drops under a given applied voltage during electrospinning, was used to understand the processing ability. As shown in Fig. 2, within the operating voltage range, the critical volume rate varied between 0.2 and 2.3 ml/h, and the volume rate value showed an increase with increased voltage applied. Based on the volume rate value, the highest rate of producing dry nanofibers from the needle electrospinning system was 0.018 and 0.207 g/h for the applied voltage of 8 and 24 kV, respectively.

The average fiber diameter under the critical electrospinning condition is also shown in Fig. 2. With the increase in the applied voltage from 8 to 16 kV, the average fiber diameter increased. Increasing the applied voltage led to a slight reduction in the average fiber diameter. The variation of fiber diameter in the applied voltage range (8–24 kV) was between 353.4 ± 85 and 413 ± 48 nm.

The average diameter of nanofibers electrospun from PVA solutions of different concentrations is shown in Fig. 4. Under the same applied voltage, with the increase in the PVA concentration, both the average fiber diameter and diameter distribution increased slightly. For comparison, the diameter data of the nanofibers electrospun by the needle electrospinning under the optimized conditions, which produced the finest nanofibers, is also shown in Fig. 4. With the same PVA concentration, the nanofibers from conical coil nozzle always had smaller average fiber diameter. The coil-electrospun nanofibers from most PVA solutions had slightly narrower diameter distribution than the needle-electrospun ones, except for 8% PVA solution which showed a reversed result. As the needle electrospinning used a much lower applied voltage range than the needleless one, the coarser fibers electrospun from the needle electrospinning setup should not derive from the nozzle structure. The difference in the electric strength around the nozzle surface and entire electrospinning zone would be the major reason leading to the difference in fiber fineness. It was reasonably expected that finer nanofibers could be produced if the applied voltage in the needle electrospinning was increased to as high as that used in the needleless electrospinning, supposing that no "corona discharge" happened in the electrospinning process.

To understand the aforementioned electrospinning result, the electric field intensity profiles of the two nozzles were calculated from the finite element analysis (FEMLAB3.4). As shown in Fig. 5, the conical wire coil gives concentrated field lines around the wire surface because of its small radius of curvature. The concentrated

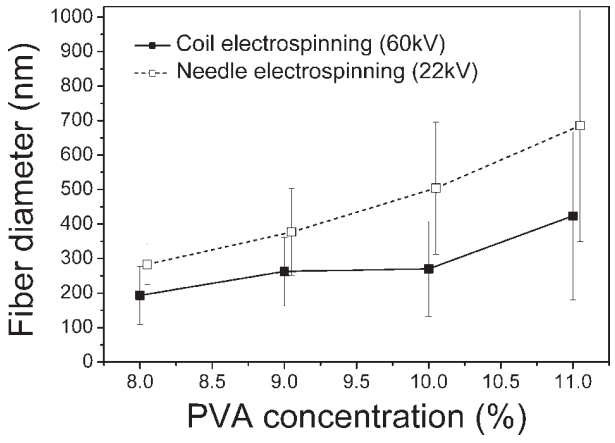

FIG. 4. Diameter of nanofibers from traditional and wire-coil electrospinning with different PVA concentrations. Collecting distance = 15 cm.

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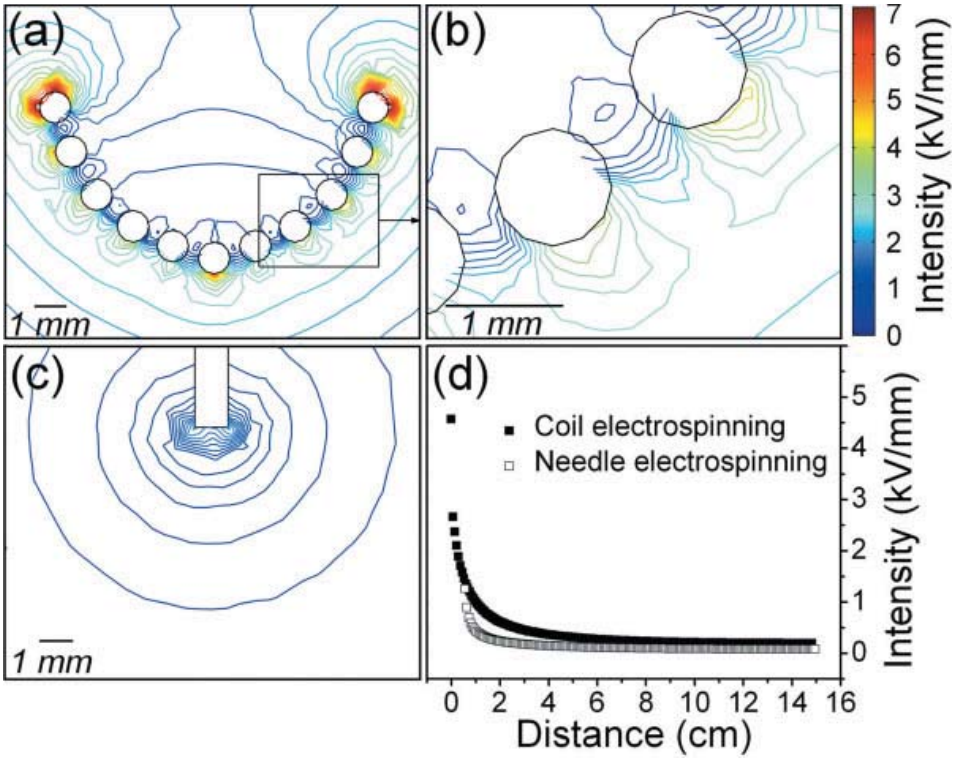

FIG. 5. Cross-sectional view of electric field intensity profiles on (a, b) conical coil nozzle ($V = 60$ kV) and (c) needle nozzle ($V = 22$ kV); (d) electric field intensity profiles along the electrospinning direction. Nozzle (0, 0); collector (0, 15).

field lines are also formed between the adjacent wires, except that the field intensity is less than on the wire surface. Similar to the conical coil, the needle nozzle also gives concentrated field lines at its tip. Under the respective applied voltage, the electric field intensity on the coil wire surface is higher than that on the needle tip. As the electric filed is the main driving force to initiate the formation of polymer jet [13], a polymer solution charged by an electric field of a higher intensity is easier to generate jets, and the jets should be stretched under stronger forces, thus producing finer fibers. In addition, both systems show similar electric filed profile from nozzle to the collector, suggesting that jets could be drawn under a similar electric field, therefore resulting in similar fiber morphologies.

Besides the electric field, the solvent evaporation from the filaments could be another factor influencing the fiber fineness. Wet filaments undergoing a longer stretching period can lead to finer fibers. For the needleless electrospinning process, multiple jets/filaments evaporate more solvent (water) to the air. As a result of increased humidity in the collecting local, further solvent evaporation from the later spun filaments could be slowed down, thus leading to finer fibers. Based on the SEM image (see Fig. 3), the nanofibers produced by the needleless setup look well isolated. This suggested that the fibers had already been dry before they deposited onto the collector. Also, the multiple jets/filaments and associated solvent evaporation did not induce the "corona discharge," presumably because the volume of water evaporated was very low and the air exchange between the electrospinning zone and ambient environment was able to maintain the humidity at a low level during the electrospinning process.

CONCLUSIONS

Electrospinning of PVA nanofibers using a conical wire-coil nozzle gives much higher fiber productivity and the resultant fibers are finer than that from a conventional needle-based electrospinning system. The novel concept of using wire coil as the electrospinning nozzle will contribute to further development of a new large-scale needleless electrospinning system for nanofiber production.

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