Effect of Experimental Parameters on Needleless Electrospinning from a Conical Wire Coil

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ABSTRACT: In this study, a conical wire coil was used as spinneret to launch a novel needleless electrospinning. Multiple polymer jets were observed on the surface of the coil in the electrospinning process. Productivity of the nanofibers can be enhanced to >2.5 g/h by using this novel nozzle. The fiber productivity and diameter together with diameter distribution were dependent on the concentration of the polymer solution, applied voltage, and collecting distance. This novel concept of using wire coil as the electrospinning nozzle depicts a model of large-scale needleless electrospinning system for nanofiber production. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3703–3709, 2012

Key words: nanofiber; needleless electrospinning; coil

INTRODUCTION

Conventional electrospinning setup comprises a syringe from which nanofiber is drawn out. The extremely low fiber production rate (usually 0.01–0.1 g/hr[1]) has confined the application of this technology in industry. Nanofiber is currently studying in both academy and industry for which has unique properties (such as high surface area and porosity) and can be applied in many different area.[2,3] Advanced technology with scaled up production rate of nanofibers is important for both research and industry.

Researchers have tried to improve the productivity of nanofiber production in electrospinning. A straightforward method is based on increasing the number of needle nozzles.[4–6] However, the multi-needle 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 can be minimized and the associated uneven fiber deposition can be avoided. Besides, clogging may frequently happen during the spinning process of multiple needle setup, which make the production incontinuous and a big effort must be put to clean the needles. Recently, needleless electrospinning setups have been developed.[7–10] The pioneering work was reported by Yarin and Zussman[8] who used a magnetic fluid to agitate the uppermost polymer solution thus to initiate the concurrent production of multiple jets from a flat polymer solution surface. Jirsak et al.[9,10] described the generation of multiple jets from a spinning surface to reach a high spinning capacity. A rotating charged electrode was used as spinneret while part of its circumference was immersed in polymer solution to pick up polymer solution onto the electrode. The other part of the circumference near to the counter electrode was the spinning surface where jets were generated from. This technology was subsequently commercialized by Elmarco under the brand name of Nanospider^{TM}. Dosunmu et al.[11] reported the formation of multiple jets from the surface of a porous polyethylene tube, in which nylon 6 solution was electrified and pushed by air pressure through the walls. Later on, Varabhas et al.[1] modified the tube wall to control the launching locations of the jets. A flat spinneret with three holes was also proposed by Zhou et al.[12,13] to generate multiple jets electrospinning. More recently, Lu et al.[14] used a rotating cone to generate needleless electrospinning with high production rate. The main difference of needleless electrospinning compared with needle electrospinning is the spinneret. In needle method, the electric field is concentrated on the tip of the needle, whereas for needleless electrospinning, the electric field is normally concentrated in a large area, thus more jets could be produced at the same time.

The generation of multiple jets from needleless electrospinning has been explained as that 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.[7] Therefore, the formation of jets in needleless electrospinning will be highly influenced by the electric field intensity around the spinneret and the electric field intensity profile in the electrospinning

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zone. Careful selection of spinneret shape and dedicated design of the geometry of the spinneret would increase the amount of jets in needleless electrospinning; fiber production rate can be improved subsequently. For instance, a comparison study of disc and cylinder electrospinning[15] has shown that disc nozzle was better than cylinder to produce thinner nanofibers with higher productivity. Previous studies about porous spinnerests[1,11–13] could increase the production rate to a certain level, for instance 5 g/h,[11] this showed great potential in industrial application of nanofiber production. But the fiber produced showed wider diameter distribution than needle eletrospinning,[11] which was not good for further application in which uniform fibers were welcomed. A proper spinneret with dedicated geometry (small in size but efficient) to produce highly uniform nanofibers with acceptable production rate would be of great importance in the development of needleless electrospinning.

Previously, a conical wire coil were used to generate needleless electrospinning,[16] it can concentrate much higher electric field on the surface of the coil and thus produce not only fibers in a larger quantity but also finer nanofibers than the needle based electrospinning system. The experimental parameters have great influence on the as-spun fiber size and production rate. Detailed study on how to control the fiber morphology (such as fiber diameter and diameter distribution) and maximize the productivity is important for further application of this technology in large scale. In this article, the effects of experimental parameters on the conical wire coil electrospinning were investigated in detail, this kind of needleless electrospinning has shown great potentials in large-scale production of nanofibers for both industry production and laboratory research.

EXPERIMENTAL

Materials and measurements

Polyvinyl alcohol (PVA) (average molecular weight 146,000–186,000, 96% hydrolyzed) is obtained from Aldrich-Sigma, US.

The fiber morphology was observed under a scanning electron microscope (SEM, Leica S440) with acceleration voltage 15 kV and working distance 10 mm. The average fiber diameter was calculated from the SEM photos with the aid of an image analysis software (Image*Pro* + 4.5), more than 100 fibers were tested from at least four SEM photos which were taken from different places of a given sample, results were averaged and standard deviation was calculated to show the diameter distribution range.

The flow rate of the needleless electrospinning was tested by measuring the time to electrospin 1-mL polymer solution. Productivity of needle electrospinning was calculated from the flow rate (mL/h) of polymer solution by the following equation:

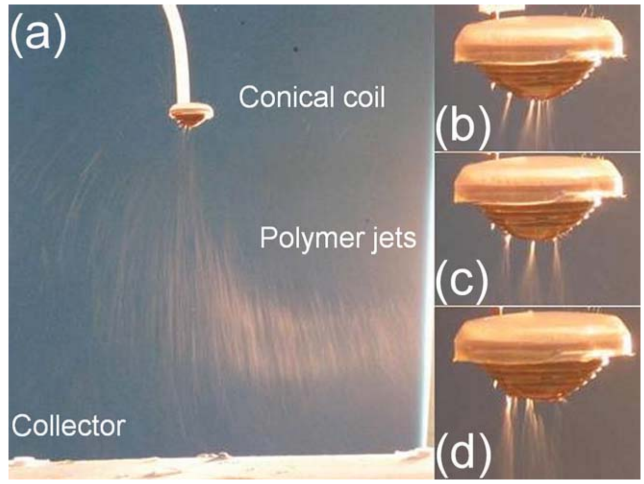

Figure 1 Photos of the wire coil electrospinning setup during the spinning process (a) and magnified view of the coil at different time (b–d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\text{Productivity} = \text{Flow rate} \times \text{PVA concentration}$$

Needleless electrospinning

Details of the wire coil needleless electrospinning setup can be obtained from previous reference.[16] A conical wire coil (cone angle = 120, wire diameter = 1 mm) was used as the electrospinning nozzle instead of needle. Conventional electrospinning parameters were set as PVA concentration 9 wt %, applied voltage 60 kV, and collecting distance 15 cm. Polymer concentration, applied voltage, and collecting distance were also changed to see their effects on the needleless electrospinning.

RESULTS AND DISCUSSION

Spinning process

Figure 1 shows the views of the ongoing needleless electrospinning. The nozzle was filled with polymer solution and then little amount of the fluid was observed on the small slits between the wires due to the drawing of the electrical force and the gravity of the polymer itself. The solution won't drop down due to the holding effect of the cone, surface tension, and the viscosity of the polymer itself. When applied voltage reached to around 40 kV, many jets were drawn out from either the surface of the wire or the gap between neighboring wires in the bottom area of the nozzle, as shown in the insets of Figure 1. This was probably due to the distribution of the electrical filed which made the electrical force at the bottom of the nozzle quite high. Because of gravity, polymer solution gathered at the bottom of the nozzle where highly concentrated electric field was formed, polymer jets were then produced when the electric force overcame the surface tension and viscosity of the solution. It was observed 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.

Productivity

For a conventional needle electrospinning, the flow rate of the PVA solutions is always controlled as 0.5–1.5 mL/h[17] so as to maintain a droplet at the tip of the needle. Too higher flow rate will make the droplet drop out quickly. Compared with needleless electrospinning, more jets were produced at the same time; the flow rate enhanced swiftly and thus the productivity increased to a much higher level. However, the flow rate couldn't be controlled in needleless electrospinning, it could be tested by calculate the time to finish a certain amount of polymer solution under different experimental conditions. The productivity can then be calculated indirectly according to equation shown in "Experimental" section.

Figure 2 shows the productivity of nanofibers of the needleless electrospinning used in this study. It was obvious that the productivity varied greatly under different applied voltage and PVA concentration when the collecting distance was 13 cm. Under a given applied voltage, lower productivity was observed when using relatively higher polymer concentration. This was probably due to the increase of viscosity of PVA solution which made the drops at the slits of the wire nozzle harder to be drawn out, and thus the flow rate decreased greatly. This was more evident when applied voltage was 7 kV, under which the differences in the ability to drawn fibers from the nozzle under different PVA concentrations made the productivity change evidently.

Besides, the productivity increases as the applied voltage increases. When the applied voltage was extremely low, such as 45 kV, the drawing strength was not strong enough to draw more jets from the nozzle, thus just few jets produced and the spinning was not continuous. It was quite evident in experimental that much more jets were observed at higher voltages.

In some other cases, when applied voltage was 60 kV and polymer concentration 9 wt %, the productivity increase from 1.18 to 2.95 g/hr when collecting distance was decreased from 20 to 10 cm. This is due to the increase of electric field intensity with the decrease of collecting distance.

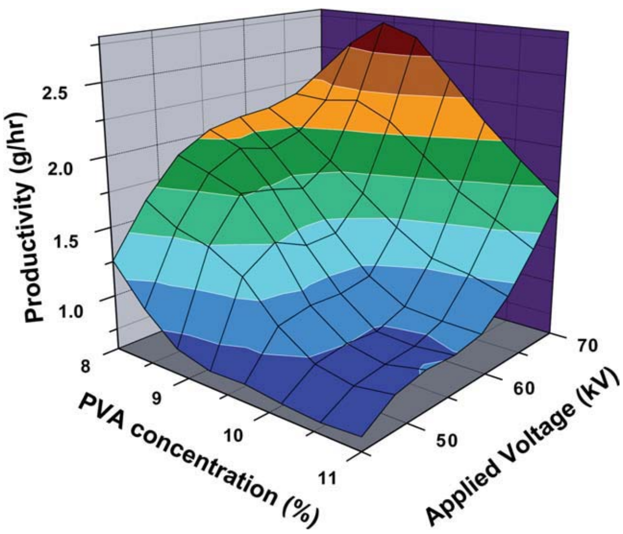

Figure 2 Productivity of wire coil needleless electrospinning with different PVA concentration and applied voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the flow rate for conventional needle electrospinning is about 0.5–1.5 mL/hr, suppose 9 wt % PVA polymer solution to be used, and then the productivity is around 0.045–0.135 g/h. The productivity of conical wire coil needleless electrospinning is 0.74–2.75 g/h under different applied voltages and 9 wt % solution, is then around 20–60 times higher than needle electrospinning.

Effect of PVA concentration

PVA concentration was changed to show its effect on the spinning process and other parameters were set as applied voltage 60 kV and collecting distance 15 cm. Figure 3 shows the surface morphology of electrospun PVA nanofibers with different PVA concentrations. It is obvious from these SEM photos that the diameter of all the electrospun PVA fibers is under 1 micron. When the PVA concentration is 8%, as shown in photo Figure 3(a), most fibers are extremely small (around 200 nm). While the concentration rises to 11%, the as-spun fibers are uneven and some of the diameter of some fibers is near 1 micron, obviously many coarse fibers were produced under this polymer concentration.

The diameter distribution of the nanofibers with different PVA concentrations was illustrated in Figure 4. When PVA concentration was 8% and 9%, the majority of the fibers diameter is distributed around 200 nm. Much wider range of fibers diameter distribution could be observed when PVA concentration increased to 11%, and the diameter distributes very irregularly [as seen from the inset of Figure 4(a)].

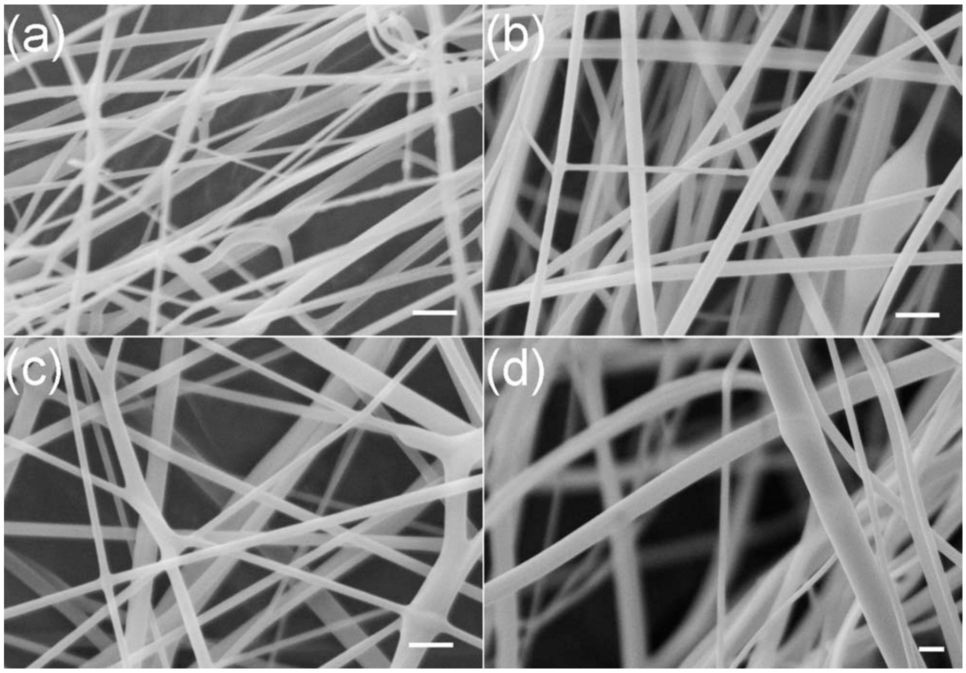

Figure 3 SEM photos of electrospun nanofibers with different PVA concentration: (a) 8%, (b) 9%, (c) 10%, and (d) 11%. Bar = 1 μm.

Diameter analysis shows the mean diameter and standard deviation of the nanofibers in Figure 4(b). It is evident that coarser fibers are produced with the increase of PVA concentration. Especially when PVA concentration changes from 10% to 11%, the mean diameter increases from 270 nm to 424 nm, and the standard deviation changes from 140 to 243. As the increase of PVA concentration led to the increase of viscosity and polymer mass of solution, fibers were less stretched in the whipping motion of the jets, the mean diameter increased accordingly.

In the needle method of electrospinning, the voltage applied shouldn't exceed 30 kV so as to protect the top point of the needle up from discharging. However, in our needleless electrospinning system, extremely high voltage (up to 70 kV) could be applied without discharging problem. Higher voltage induced stronger electrical field which provides higher driving force in the formation of jets, which will increase the attenuating of the as-spun fibers, so the nanofibers from needleless electrospinning show lower diameter (from 193 ± 84 nm to 424 ± 243 nm with PVA concentration 8–11 wt %) compared with that from needle electrospinning (from 283 ± 59 nm to 685 ± 336 nm with PVA concentration 8–11 wt %).[16]

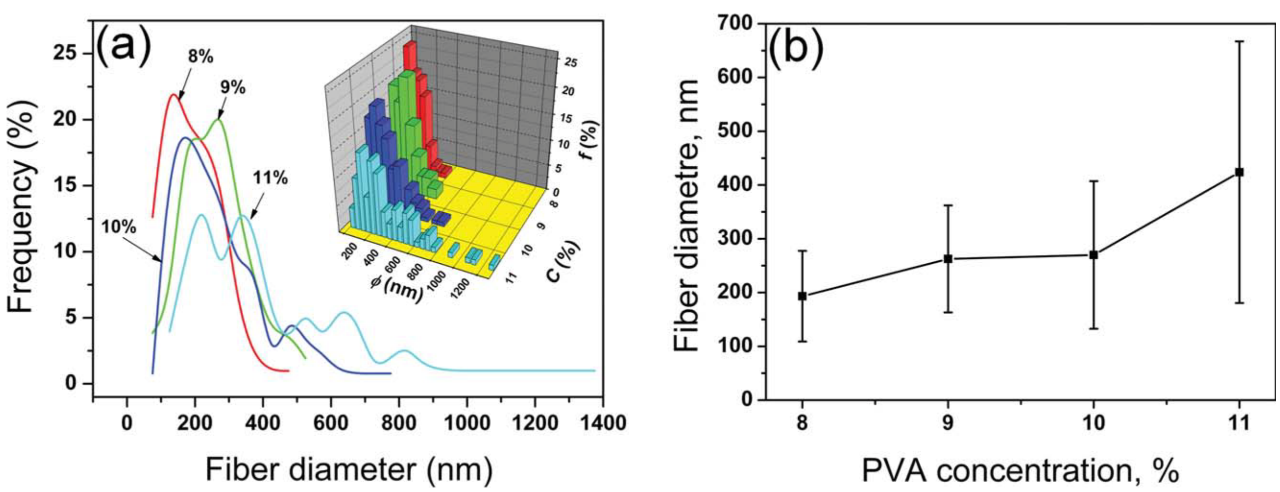

Figure 4 Diameter distribution (a) and mean diameter with deviation (b) of electrospun nanofibers with different PVA concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

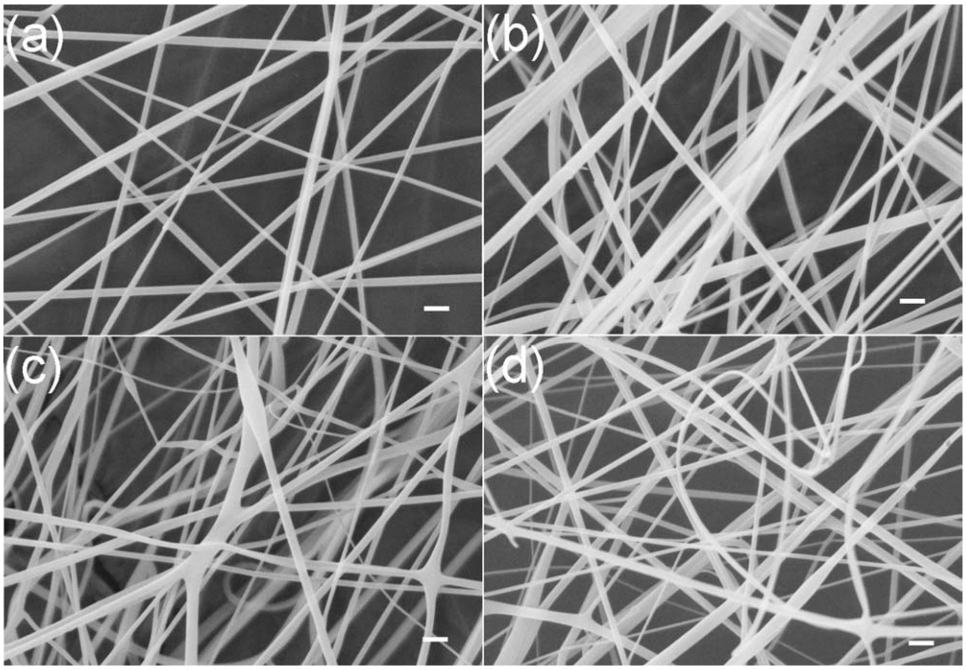

Figure 5 SEM photos of electrospun nanofibers with different applied voltage: (a) 45 kV, (b) 50 kV, (c) 60 kV, and (d) 70 kV. Bar = 1 μm.

The larger standard deviation in the analysis is mainly due to the existence of an amount of fibers with larger fiber diameter. In multi-jets electrospinning, solution drops were larger than that of needle methods which incurred big amount of larger fibers and thus increased the standard deviation.[9] In our study, the dripping problem could be solved by decrease the wires gauge of the nozzle and increase applied voltage. For instance, a gap distance of <1 mm between neighboring wires worked well when PVA concentration was 9 wt %. A relative bigger gap could be used when high concentration was applied and the gap couldn't be too small, for example, <0.5 mm, under which no polymer solution was leaking out. Besides, when voltage increased to high level, polymer solution will not accumulate in the spinneret but was drawn out swiftly, which decreased the chance of forming drops. Thus, the standard deviation is much lower than that of needle electrospinning.

Effect of applied voltage

Applied voltage was changed in experimental to show its effect on the morphology and diameter of PVA nanofibers, PVA concentration was set as 9 wt % and collecting distance was 15 cm. Figure 5 shows the SEM photos of the PVA nanofibers under different applied voltages. It is evident that the diameter of most nanofibers is under 500 nm, and most fibers are <200 nm.

Figure 6(a) illustrates the diameter distribution of nanofibers with different applied voltages. All the distribution curves show a main peak at about 200 nm except for 45 kV whose main distribution peak was around 300 nm. Diameter analysis of all the samples is indicated in Figure 6(b). When applied voltage increased from 45 kV to 50 kV, the mean diameter of nanofibers decreases dramatically from 325 nm to 275 nm, after that, the diameter decreases slightly and then keeps stable with the increase of applied voltage. Although increased voltage strengthens the electrical field during the electrospinning process, extremely higher voltage (above 60 kV) shows less impact on the attenuation of nanofibers. This was quite different from needle electrospinning in which applied voltage showed great influence on fiber diameter. It was obvious that at the beginning stage, for instance <60 kV, strengthening of electric field had great effect on the attenuation of polymer jets due to the increased electrostatic force. Further strengthening of the electric field showed little effect, this was probably due to the properties of the polymer which made the further attenuation of the jet impossible, thus the diameter was unchanged. Besides, the standard deviation decreases slowly with the increase of applied voltage, this is probably due to the higher stretching of the jets under higher voltage.

Effect of collecting distance

The collecting distance was also changed in experimental to show its effect on the morphology and diameter of nanofibers, other experimental parameters

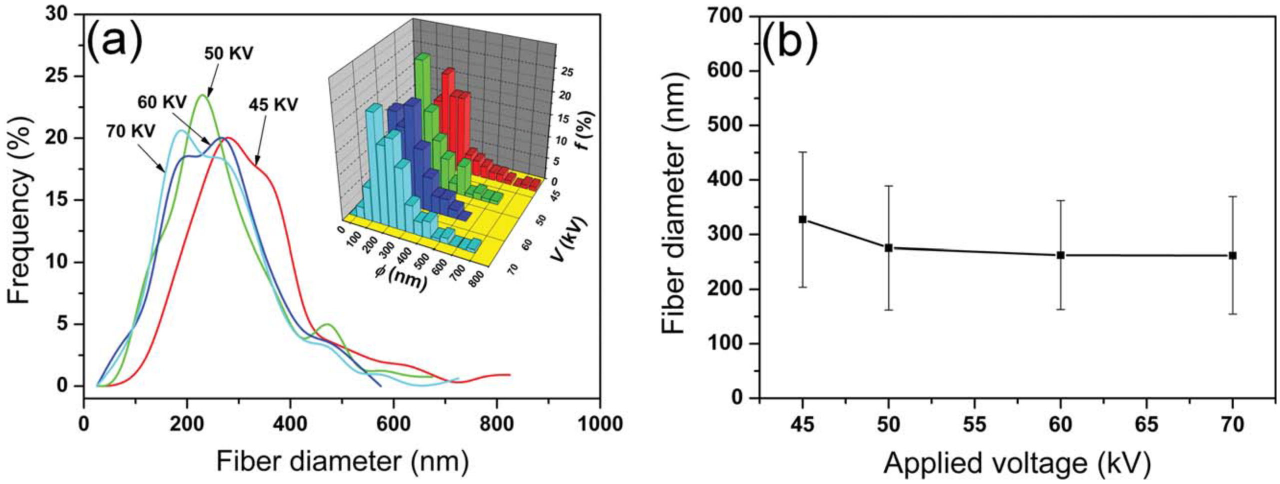

Figure 6 Diameter distribution (a) and mean diameter with deviation (b) of electrospun nanofibers with different applied voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were set as applied voltage 60 kV and PVA concentration 9 wt %. Figure 7 shows the SEM photos of PVA nanofibers under different collecting distances; from these photos, all the nanofibers are very thin with diameter much lower than 1 micron, no much difference could be observed from these three photos except for Figure 7(a), in which there are some nanofibers with larger diameter than others.

The diameter distribution of nanofibers with different collecting distances is shown in Figure 8(a), the distribution of fibers with collecting distance 10 cm and 15 cm looks similar with a main peak around 200 nm, but the curve of 10 cm shows some small peaks after 500 nm [evident from inset of Figure 8(a)]. The main peak of nanofibers with collecting distance 20 cm is around 300 nm, which was greater than that with other collecting distances.

Diameter analysis based on the SEM photos of these samples show many differences in Figure 8(b). When collecting distance changes from 10 cm to 15 cm, nanofibers diameter decreases and so does the standard deviation. However, when the collecting distance increases from 15 cm to 20 cm, the nanofibers diameter jumps to a higher level which is even higher than that of 10 cm, and the standard deviation deteriorates again. When the collecting distance

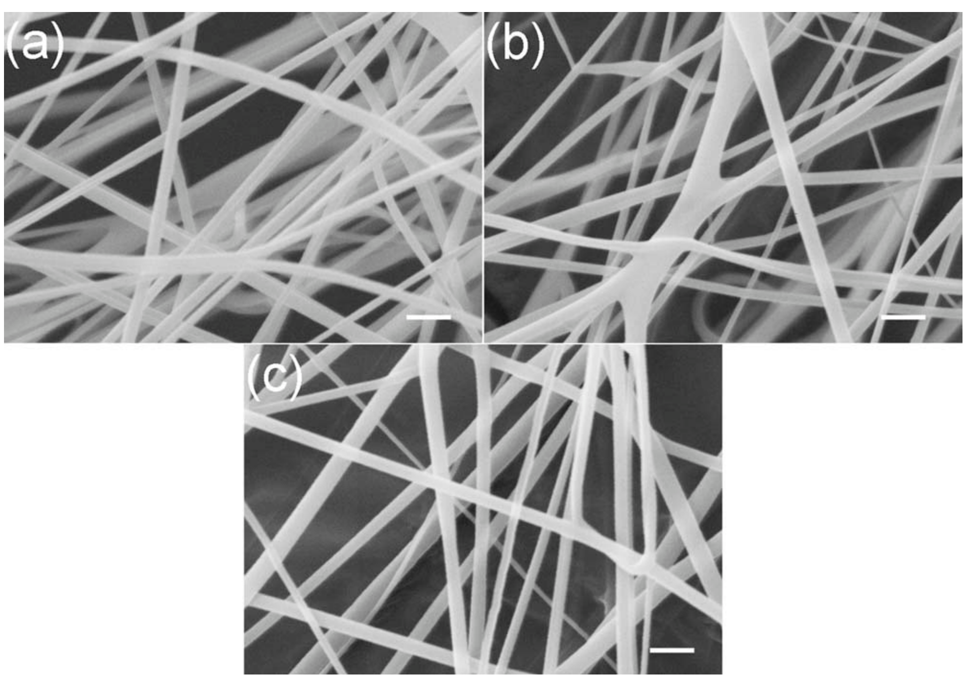

Figure 7 SEM photos of electrospun nanofibers with different collecting distance: (a) 10 cm, (b) 15 cm, and (c) 20 cm. Bar = 1 μm.

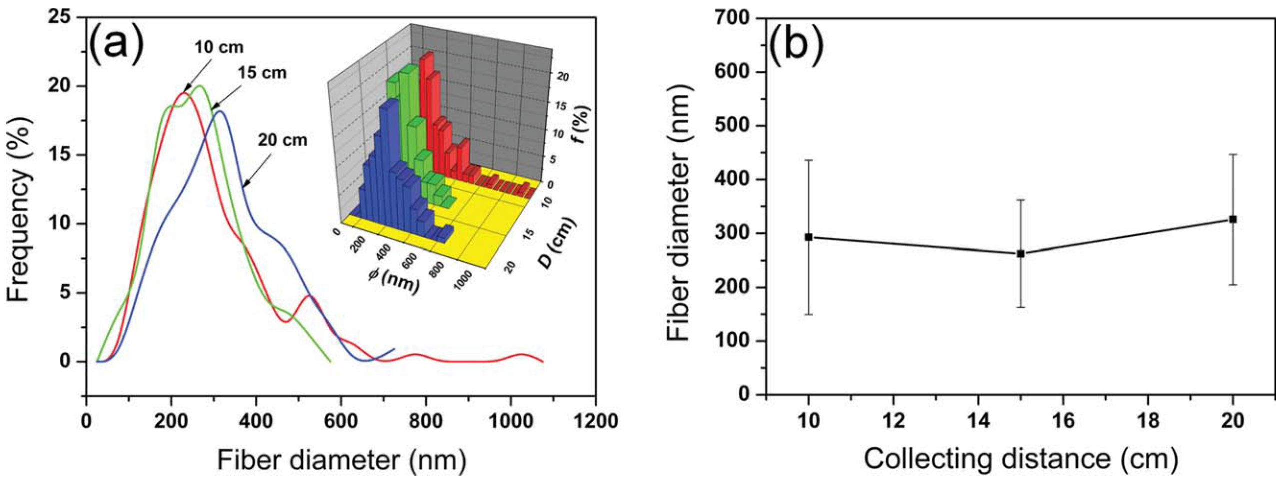

Figure 8 Diameter distribution (a) and mean diameter with deviation (b) of electrospun nanofibers with different collecting distance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is too short (10 cm) to make the jets stretch enough in the whipping process, the as-spun fibers shows larger mean diameter together with wider deviation. Increase the collecting distance could improve the whipping and thus the attenuation effect of nanofibers. However, with the increase of collecting distance, the electrical field intensity decreases greatly which affects the drawing effect of fibers in the jet formation. In experimental, when collecting distance was set as 20 cm, fewer jets were observed compared with that under shorter collecting distances, and some PVA solution tended to accumulate in the gap between the wires of the screw nozzle. In some cases, when the accumulated solution was not exhausted for a long time, dripping happened and the dropping solution broke into several coarse jets, which incurred the formation of coarse fibers.

CONCLUSIONS

A conical wire coil was successfully used to generate needleless electrospinning of PVA nanofibers. Multiple polymer jets were produced on the surface of the coil during the spinning process. The productivity of this needleless electrospinning was 20–60 higher than that of needle electrospinning, and the productivity was greatly increased by increase of applied voltage and decrease of collecting distance under a given polymer concentration. Under a given applied voltage and collecting distance, the productivity decreased with the increase of PVA concentration due to its higher viscosity. The fiber diameter and diameter distribution was greatly influenced by the experimental parameters like PVA concentration, applied voltage, and collecting distance. This novel concept of using a conical wire coil nozzle will contribute to further development of large-scale needleless electrospinning system for nanofiber production.

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