Rapid Communication

Polymer nanofibers prepared by low-voltage near-field electrospinning*

Zheng Jie(郑 杰)[a], Long Yun-Ze(龙云泽)[a)b)†], Sun Bin(孙 彬)[a], Zhang Zhi-Hua(张志华)[a], Shao Feng(邵 峰)[a], Zhang Hong-Di(张红娣)[a], Zhang Zhi-Ming(张志明)[c], and Huang Jia-Yin(黄家寅)[a)‡]

[a] *College of Physics Science, Qingdao University, Qingdao* 266071, *China*

[b] *State Key Laboratory Cultivation Base of New Fiber Materials and Modern Textile, Qingdao University, Qingdao* 266071, *China*

[c] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao* 266100, *China*

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Electrospinning is a straightforward method to produce micro/nanoscale fibers from polymer solutions typically using an operating voltage of 10 kV–30 kV and spinning distance of 10 cm–20 cm. In this paper, polyvinyl pyrrolidone (PVP) non-woven nanofibers with diameters of 200 nm–900 nm were prepared by low-voltage near-field electrospinning with a working voltage of less than 2.8 kV and a spinning distance of less than 10 mm. Besides the uniform fibers, beaded-fibers were also fabricated and the formation mechanism was discussed. Particularly, a series of experiments were carried out to explore the influence of processing variables on the formation of near-field electrospun PVP nanofibers, including concentration, humidity, collecting position, and spinning distance.

Keywords: nanofibers, near-field electrospinning, beaded-fibers

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1. Introduction

One-dimensional (1D) nanostructures such as nanotubes, nanowires, and nanofibers have drawn much attention due to their unique physical and chemical properties and potential applications in nanoscale devices.[1−7] Among a variety of synthesis methods, electrospinning has been recognized as a simple, efficient technique for the fabrication of polymer and ceramic nanofibers.[5−7] The practical apparatus of electrospinning, via which a charged jet of polymer solution is deposited onto a collector under the action of an electrical field, dates back to 1934.[8] For the feasibility of contracting long and continuous polymeric fibers with diameters typically ranging from a few micrometers down to 10 nm or less, electrospinning has been extensively studied in the last decade.[5−7,9−19] In a traditional process, the polymer solution is extruded from the orifice of a needle in presence of a high-voltage electric field. Herein, the dc voltage used is usually of 10 kV–30 kV and the jet travels 10 cm–20 cm in air before it drops onto the collector. During this course, most of the solvent evaporates away. Then the electrospun nanofibers can be collected as non-woven mats on the grounded collector.[9−12] The electrospinning process is unstable in nature as it relies on the chaotic whipping of liquid jets to generate nanofibers, and other factors, such as concentration, humidity, spinning voltage, and distance can also influence it.

Near-field electrospinning[13−19] is a modified spinning method for fabricating micro- and nanoscale fibers, which is similar to traditional electrospinning in its setup and basic principle. However, the voltage and the spacing become smaller in near-field electrospinning than those in traditional electrospinning. There are several publications that describe the possible applications taking advantage of the straight electrospinning process for the short distance between electrode and collector before the fibers stretch. For example,

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†Corresponding author. E-mail: yunze.long@163.com

‡Corresponding author. E-mail: wlxhuang@163.com

with a 1-mm long, micro-fabricated scanned triangular tip as electrospinning source, Kameoka *et al.*[14] have obtained oriented polyethylene oxide nanofibers with diameters ranging from 100 nm to 1800 nm, and the tip surface was coated by gold to increase its conductivity. Sun *et al.*[15] used a tungsten electrode tip with diameter of 25 μm to fabricate nanofibers with 50 nm–500 nm line width, and in this case, the minimum applied voltage was 600 V, and the minimum electrode-to-collector distance was 500 μm. In addition, Wu *et al.*,[19] by means of an atomic force microscope (AFM) based voltage-assisted electrospinning technique, obtained the polyethylene oxide (PEO) polymeric single fibers with nanometer scale diameters. Here the voltage was from 8 V to 12 V and the spinning distance between the tip and the substrate was set from 10 μm to 20 μm.

By near-field electrospinning, nanofibers could be collected precisely or orderly, and which makes this technique a potential tool in many fields such as direct write nanofabrication,[15,18] large area deposition of orderly nanofiber patterns,[13] high precision deposition of a nanofiber,[16,17] chip-to-chip fluidic connectors, and networks in micro-electromechanical system (MEMS) applications including BioMEMS, microfluidics.[20] All the reported publications mentioned above usually used a micro-scale probe as the spinning tip, which was complicated and expensive for operation and fabrication. In addition, the effect of processing variables on the morphology of near-field electrospun nanofibers has not been explored intensively.

In the conventional vertical electrospinning configuration, a large droplet of spinning solution usually appears on the collector due to the action of gravity, which just covers or drowns most of the electrospun nanofibers. In order to observe the nanofibers clearly, a horizontal electrospinning configuration was used in this paper. Namely, we put the spinning tip and collector in a horizontal line instead of in a vertical line so that the solution droplet can be separated from the electrospun fibers. In this way, polyvinyl pyrrolidone (PVP) non-woven fibers with diameters of 200 nm–900 nm were prepared by a low-voltage near-field electrospinning with a working voltage of less than 2.8 kV and spinning distance less than 10 mm. Besides, beaded fibers among the non-woven fibers on the collector were also obtained and the formation mechanism was discussed. Moreover, we carried out a series of experiments to explore the influence of concentration, humidity, and spinning distance on morphologies and structures of the near-field electrospun fibers.

2. Experimental details

The schematic illustration of the used setup for near-field electrospinning is shown in Fig. 1. The spinning metal needle was connected to the positive electrode of a high-voltage dc power supply (DW-P403-1ACCC, Tianjin Dongwen), and a dc voltage was supplied. The grounded collector, a piece of flat aluminum foil, was placed less than 10 mm to the tip of the needle. When the electric field force overcomes the surface tension, the polymer solution begins to flow as jets towards the collector. Before reaching the collector, the charged jets are stretched and/or split to form micro- or nanoscale-fibers due to the strong electric field, bending instability, and mutual repulsion, and most of the solvent evaporates away.[9,10,21]

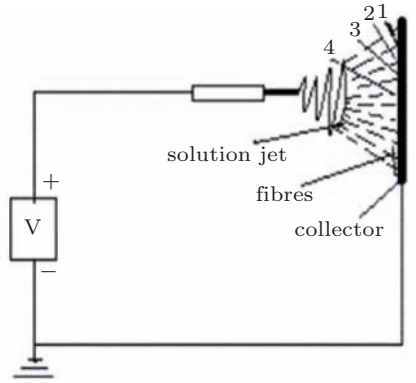

Fig. 1. Schematic illustration of the used setup for near-field electrospinning. Numbers 1–4 denote different positions to observe fibers as stated in Fig. 2.

Ethanol (Yantai Sanhe) was used as the solvent, the polymer, PVP (average molecular weight of 10000, Shanghai Aibi) were dissolved in this solvent at different concentrations of 20, 25, 30, 35, and 40 wt%, respectively, under stirring for 2 h at room temperature. A scanning electron microscope (SEM; JSM-6390) was used to characterize the morphologies and structures of the electrospun fibers. All samples were coated with an evaporated gold thin film before SEM imaging to ensure high conductivity.

3. Results and discussion

In order to study the effect of processing variables on the morphology of near-field electrospun nanofibers and textiles, a series of experiments under different spinning conditions including polymer concentration, collecting position, humidity, and working distance have been carried out.

3.1. Influence of collecting position

Figures 2(a)–2(d) show the SEM images of PVP nanofibers electrospun from 25 wt% PVP solution under experimental conditions as follows: a working voltage of 2.8 kV, a nozzle-to-collector distance of 6 mm, and humidity of 40% RH at room temperature. Uniform fibers and beaded fibers were observed at different positions (e.g., position 1–4) of the collector (Fig. 1). At the edge of the collector (position 1, Fig. 2(a), the distance between position 1 and position 4 was about 0.4 mm), there were many micro-scale beads on the electrospun nanofibers. Closer to the collector center, less beaded fibers were observed. At the collector center (position 4), the structures were totally uniform fibers (Fig. 2(d)). The diameter of the non-woven fibers distributed from 200 nm to 900 nm, and the average diameter was 410 nm, as shown in Fig. 2(e).

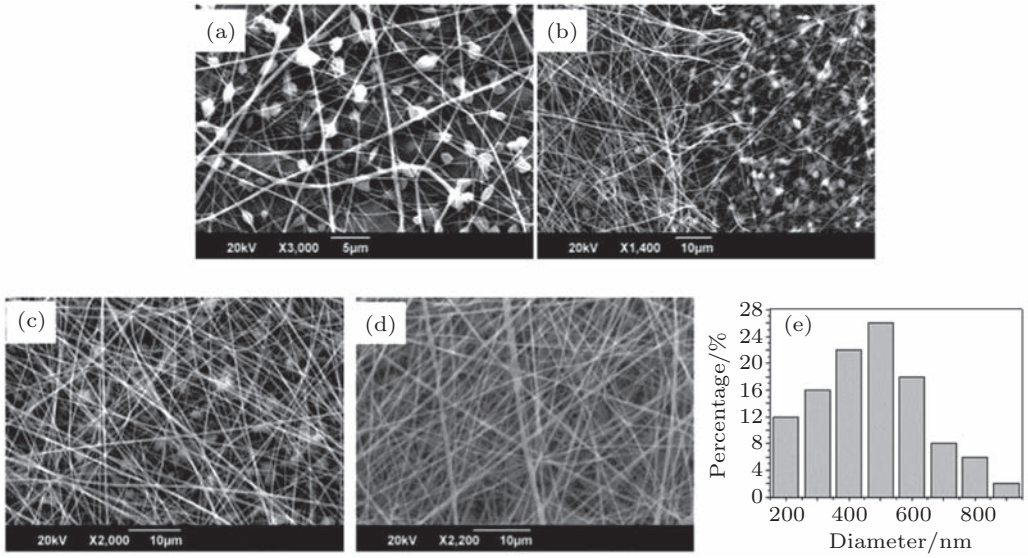

Fig. 2. 2(a)–2(d) The corresponding SEM images of the electrospun fibers deposited on positions 1, 2, 3, and 4 of the collector shown in Fig. 1; (e) diameter distribution of the non-woven nanofibers shown in panel (d).

As we know, traditional electrospun fibers often have beads as "byproducts" due to low molecular weight and viscoelasticity, which is bound up with mass fraction of the spinning solution, as well as the instability of the jet of the polymer liquids. Yarin, Entov, and Reneker *et al.* have studied the instability of a charged jet of polymer solution, and it is believed that the low viscoelasticity of the solution, charge density carried by the jet, and the high surface tension of the solution are the main factors of the formation of electrospun beaded nanofibers.[22−26] For example, the capillary instability that causes a cylindrical liquid jet to collapse into separated droplets occurs when the excess electrical charge carried by the jet is reduced. This structure solidifies to form beaded nanofibers.[11,25] In the present case, we think the instability of the spinning jets and the lower mass percentage of polymer solution are the main factors for the formation of beaded fibers. For near-field electrospinning, the nozzle-to-collector distance is very small, only several millimeters, the electric field is quite nonuniform especially at the edge of collector with a weak electric field strength, which results in the charged jet being much more instable at the edge of the collector than that in the center part, so the beaded fibers tend to appear at the edge of collector. In addition, when increasing PVP concentration from present 25 wt% to 30 wt%, beaded fibers also disappear (please see the following context).

3.2. Influence of PVP concentration

As mentioned above, the viscoelasticity, or concentration of spinning solution has a significant effect on the formation of fibers via conventional electrospinning. At low viscosities, solution surface tension is the dominant influence on fiber morphology and below a certain concentration drops will form instead of fibers. At high concentrations, electrospinning will be prohibited by an inability to control and maintain the flow of a polymer solution to the nozzle.[24] In addition, a higher polymer concentration tends to stabi-

lize the jet and results in fewer beads and more uniform fibers.[25,26] In this work, five experiments have been performed to investigate the influence of PVP concentration at room temperature under conditions of a low voltage of 2.5 kV, a nozzle-to-collector distance of 6 mm and a relative humidity of 40% RH, respectively. The PVP mass fraction of spinning solution varied from 20 wt% to 40 wt%. The results are summarized in Table 1. We can see that no fibers have been collected when the PVP mass fraction was too low (20 wt%) to attach to the spinning tip or the PVP concentration was too large (40 wt%) to produce spinning jet. However, a mixture of beaded fibers and uniform fibers was obtained when the PVP loading was 25 wt%, and totally uniform fibers were collected as the PVP concentration increased to 30 wt% and 35 wt%. It is noted that the average diameter of the non-woven fibers electrospun from 35 wt% solution was 690 nm, much larger than that from the 30 wt% solution ($\sim$ 310 nm) due to higher viscosity.

Table 1. Electrospinning results using spinning solutions with different PVP loadings.

PVP/wt%	20 wt%	25 wt%	30 wt%	35 wt%	40 wt%
Results	droplets without fibers	beaded fibers mixed with uniform fibers	totally uniform fibers	totally uniform fibers	no fibers
Morphology or reason	due to too low concentration, solution cannot attach to the spinning tip	beaded fibers mixed with uniform fibers due to lower concentration	uniform fibers with an average diameter 310 nm	uniform fibers with an average diameter 690 nm due to higher concentration	due to too high concentration, the spinning is prohibited

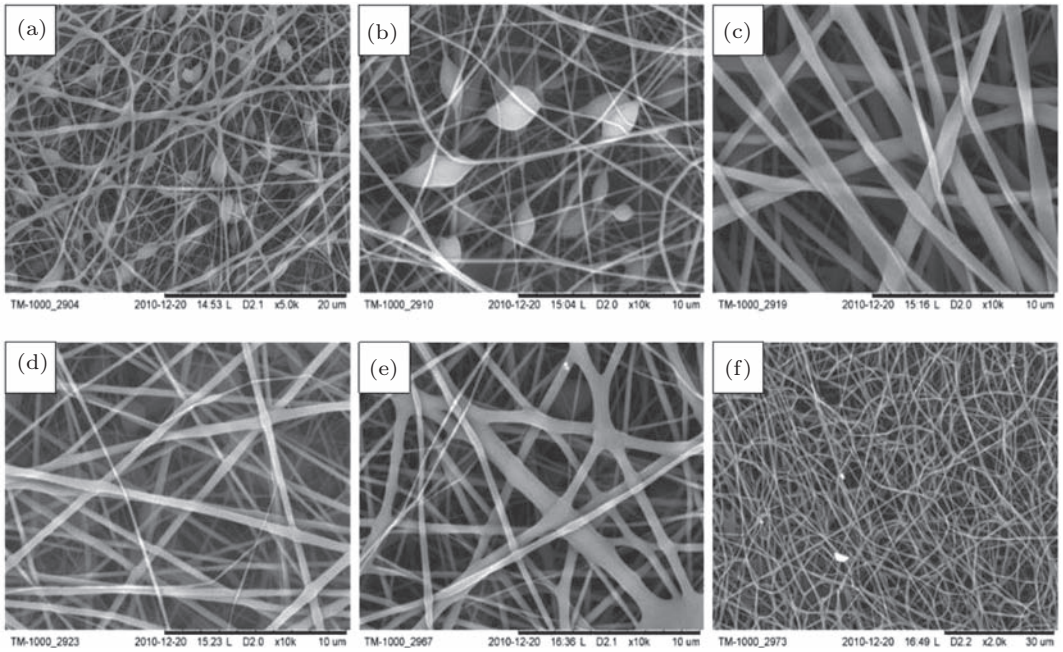

Fig. 3. SEM images of PVP fibers electrospun under different humidity: (a) 30% RH, (b) 35% RH, (c) 40% RH, (d) 45% RH, (e) 55% RH, and (f) 60% RH.

3.3. Influence of humidity

Humidity is another factor influencing the surface morphology of electrospun fibers and the formation of the beaded fibers, because the humidity can affect electrical charge carried by the jet, as well as volatilization of solvent and thus solidification process of the electrospun fibers. To explore the influence of humidity, a series of experiments were carried out at room temperature (16 °C–17 °C) under conditions of 25 wt% PVP solution, working voltage of 2.8 kV, nozzle-to-collector distance of 6 mm, and a relative humidity of 30, 35, 40, 45, 55, and 60% RH, respec-

tively. The results indicate that beaded fibers mixed with uniform fibers could be collected when the humidity was under 40% RH (Figs. 3(a) and 3(b)), and completely uniform fibers obtained when the humidity was higher than 40% RH (Figs. 3(d)–3(f). Here we note that when the humidity was 40% RH, uniform fibers were collected at the center of the collector (Fig. 3(c)) and beaded fibers were still found at the edge of the collector, just like the results shown in Fig. 2. Namely, totally uniform fibers were easily formed when the humidity was high, which may be due to slow and uniform volatilization of solvent from the jet, as well as quick conduction and balance of electric charges carried by the jet, which can help to reduce capillary instability and other instabilities. In addition, it is found that the PVP fibers became very curly and "soft" when the humidity was very high (60% RH, Fig. 3(f)) possibly owing to slow volatilization of solvent and inner stress of the jet.

3.4. Influence of spinning distance

In needle electrospinning, under the influence of electric force, the charged solution droplet at the needle tip reduces its size so that the force balance is maintained. With an increase in the applied voltage, the shape of the solution droplet evolves from the hemi-sphere to a cone shape (Taylor cone) with a high electric force concentrated at the tip of the Taylor cone. When the electric field reaches a critical voltage V_c, the droplet at the cone tip overcomes its surface tension to eject into the electric field, and a solution jet is thus generated. According to Taylor's calculation, the critical applied voltage V_c for electrospinning is given by[27]

$$V_c^2 = 4\ln\left(\frac{2h}{R}\right)(1.3\pi R\gamma)(0.09), \tag{1}$$

where h is the distance from the needle tip to the collecting screen, R is the needle outer radius,

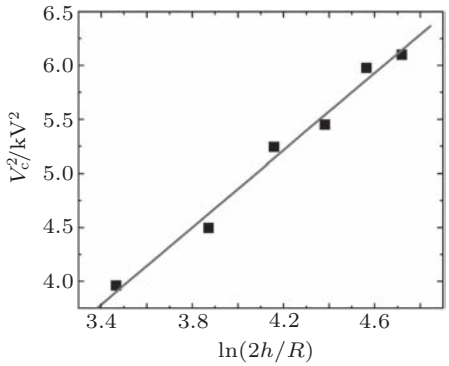

Fig. 4. Variation of the critical voltage V_c with spinning distance h.

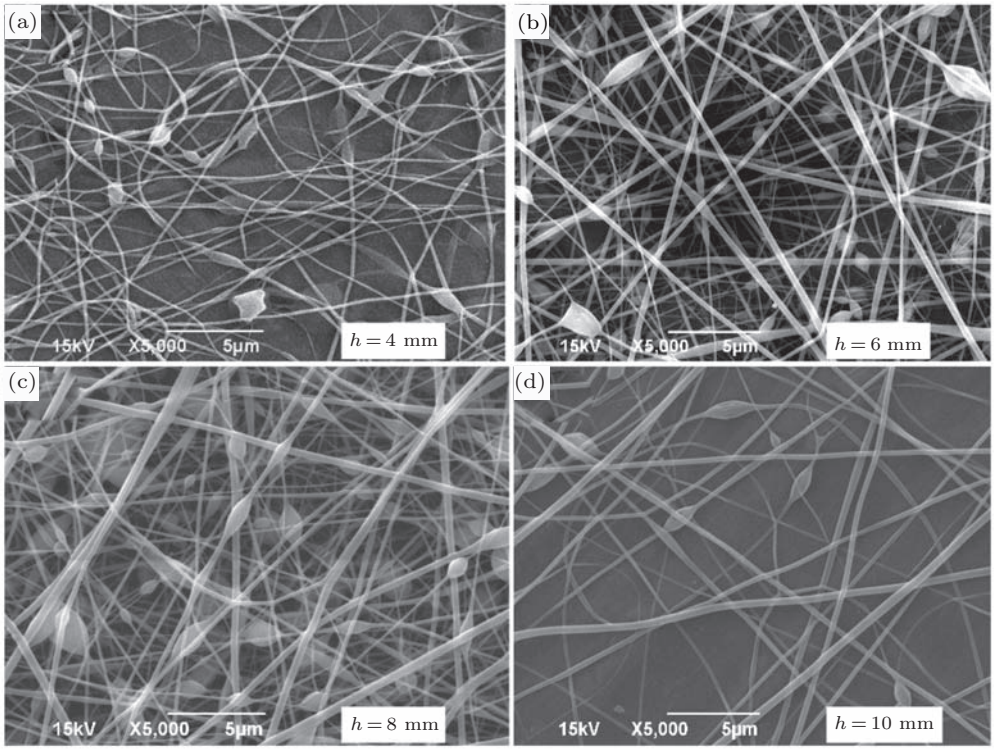

Fig. 5. SEM images of PVP fibers electrospun with different spinning distances: (a) 4 mm; (b) 6 mm; (c) 8 mm; and (d) 10 mm.

and γ is the surface tension of the solution. The factor 0.09 is inserted to predict the voltage. For low-voltage near-field electrospinning, the spinning distance h is short and can be controlled precisely. If other parameters are constant, the critical voltage V_c, the lowest voltage which can generate an electrospinning process, should have the following relationship with spinning distance h: V_c^2 is linear with $\ln(2h/R)$. So in this work, we have also studied the dependence of the critical voltage with spinning distance and its influence on fiber morphology.

In the present case, the needle outer radius R was 0.25 mm, the surface tension γ can be treated as constant due to the same solution (25 wt% PVP solution) used here. The experimental results are shown in Fig. 4. The critical voltage V_c increased from 1.99 kV to 2.48 kV when the spinning distance h increased from 4 mm to 14 mm. The linear fitting of the data $V_c^2 \sim \ln(2h/R)$ indicates that the result is qualitatively consistent with Taylor's theory. In addition, the corresponding electric field strength (estimated by V_c/h) is about 10^5 V/m, which is also the same order of magnitude as that of the traditional electrospinning. Finally, it should be mentioned that the fiber morphology was less dependent on the spinning distance. As shown in Fig. 5, beaded fibers mixed with uniform fibers were obtained in all the cases.

4. Conclusion

In summary, we carried out a series of experiments to explore the influence of processing variables on the morphology of polymer nanofibers via modified low-voltage near-field electrospinning. It is found that higher concentrations tended to result in fewer beads and more uniform fibers. Moreover, uniform fibers were easily produced under high humidity. These results indicate that the morphology of the near-field electrospun fibers can be controlled by experimental variables. And low-voltage near-field electrospinning is a promising technique which may be used in precision deposition of nanofibers for nanodevices, direct-write nanofabrication, and chip-to-chip fluidic connectors, and so on.

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