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Bubble-electrospinning for fabricating nanofibers

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ABSTRACT

Bubble electrospinning with aqueous solvent is used to fabricate nanofibers within 100 nm. The effect of applied voltage on the diameters of nanofibers is experimentally studied, revealing that the higher voltage favors the smaller diameter. Polyvinyl Alcohol (PVA) with water as solvent is used to produce environmentally benign nanofibers, and the minimal diameter reaches as small as 46.8 nm.

1. Introduction

In our research the nanofibers are defined as these continuous fibers with diameters less than 100 nm [1]. The nanofibers have many fascinating properties [2–8], such as unusual strength, high surface energy, high surface reactivity, high thermal and electric conductivity.

Electrospinning is a simple method for producing nanofibers, and has attracted much recent interest. A detailed description of the electrospinning procedure is available on the monograph [1]. The classical approach is either polymer solution [9–11] or polymer melt [12]. Solution-electrospinning has typically resulted in fibers with diameters of 100–10,000 nm, while melt-electrospinning tens of microns [12], though the electrospun fiber diameters can be reduced remarkably via mageto-electrospinning [13] or vibration-electrospinning [14,15], it is still a great challenge to reducing fiber diameters to tens of nanometers, where nano-effects [3] operate geometrically. Dragline silk consists of thousands of nano-filaments with diameter of about 20 nm [16,17], thus it can make full use of nano-effects [3]. It is a challenge to developing technologies capable of preparing for nanofibers within 50 nm. Bubble-electrospinning [18–20], which is a potential technology for mass-production of nanofibers, is uniquely qualified to address this challenge. The flexibility and adaptability provided by the method have made it a strong candidate for fabricating nanofibers on such a scale. The bubble electrospinning mimics the spider-spinning procedure [19], where spider silks are produced at close to ambient temperatures and pressures using water as the solvent. We demonstrate that PVA fiber diameters hereof could decrease to tens of nanometers using aqueous solution as the solvent. Electrospinning with aqueous solvents may be appealing for applications and configurations where toxic solvent accumulation is a concern. Environmentally Benign Manufacturing (EBM) will emerge as a significant competitive dimension between companies.

2. Bubble-electrospinning

Bubble-electrospinning was invented in 2007 [21,22]. In contrast to the classical electrospinning, of which the electrospinability mainly depends on solution properties, bubble-electrospinning's depends geometrically on sizes of produced bubbles.

Consider one bubble made of polymer solution under voltage as illustrated in Fig. 1. The net upward force on the top hemisphere of the bubble reads

$$F_{\text{upward}} = \pi r^2 (P_{\text{i}} - P_{\text{o}}) + Eq \tag{1}$$

where P_{i} and P_{o} are, respectively, the air pressures inside and outside the bubble, E is the applied voltage, q is the total surface charges above a cross-section, r is bubble radius of the cross-section.

The net downward force due to the surface tension can be written down in the form

$$F_{\text{downward}} = 2\pi r T \delta \cos\theta \tag{2}$$

where T is the surface tension per area, δ is the thickness of the bubble, θ is the angle between the tube wall and the surface tension force.

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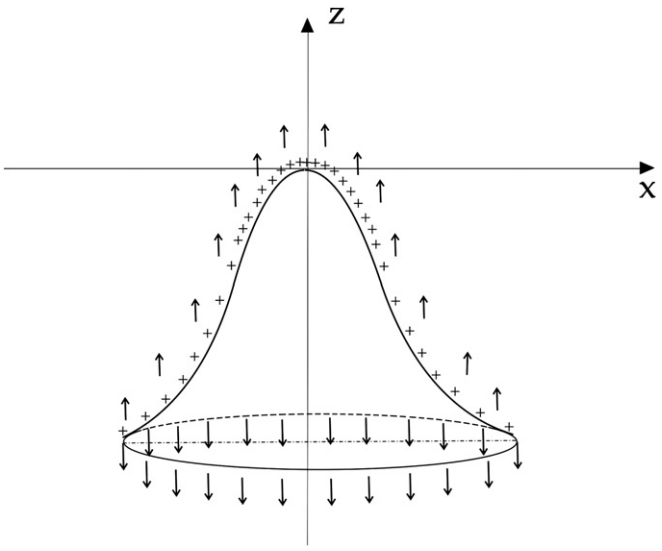

Fig. 1. Deformation of polymer bubble under electric force.

According to the force balance, $F_{\text{upward}} = F_{\text{downward}}$, we have

$$T = \frac{\pi r^2 (P_i - P_o) + Eq}{2\pi r \delta \cos\theta} \tag{3}$$

When no voltage is applied, the surface tension depends geometrically upon the size of the bubble [23]. When an electric field is present, it induces charges onto the surface of bubbles in clusters and solution surface. The surface charge coupling and the external electric field create a tangential stress, leading the deformation of the bubble into a protuberance-induced upward-directed reentrant jet, as demonstrated in Fig. 1. Once the electric field exceeds the critical value (V_0 in Eq. (4)) needed to overcome the surface tension, one fluid jet ejects from the apex of the conical bubble ($z = 0$). When the bubble is broken, the surface charges will be re-distributed, and the bubble surface was pulled upwards by electric force again, thus multiple jets are formed in a very short period.

In case the bubble size tends to nano-scale, the surface tension becomes extremely small, and it is easy to pull the nano-bubbles into nanofibers as the case in spider-spinning system [17]. This technology was demonstrated to produce nanofibers as small as 50 nm [19]. In this paper only a single bubble is used for fabrication of nanofibers, see Fig. 2.

3. Experimental

Polyvinyl Alcohol (PVA) with a degree of polymerization of 1750 ± 50 was purchased from Shanghai Chemical Reagent Co., Ltd and used without further purification. PVA debris was added into distilled water at room temperature, then the mixture was stirred at 80–90 °C for 2 h to get homogeneous and transparent solution. After cooling down to room temperature, the solution was used to produce nanofibers. 10 wt% PVA aqueous solution was prepared. A flat piece of aluminum foil placed 8 cm above the nozzle was used for collecting fibers. The voltages applied to the wire electrode were varied from 10 kV, 20 kV to 30 kV. The experimental set-up is given in Fig. 3.

This is the first time to use a single bubble to fabricate nanofibers. In our previous study, multiple bubbles with different sizes were generated on the surface of polymer solution, making it difficult to investigate the effects of spinning conditions on the properties of the nanofibers produced. In the present study we use a small tube 11.5 mm in diameter, so that only a single bubble is formed on the top of the tube. Though there are also many different bubbles on the polymer solution surface, which will be interacted with each other, as a result a single bubble is formed. The distance between the top of the tube and the solution surface is about 10 mm, and the gas-tube is imbedded under the solution surface below 5 mm.

The experiments were carried out at room temperature, 30 °C, and 69% relative humidity.

Fig. 2. Force analysis of the single bubble electrospinning.

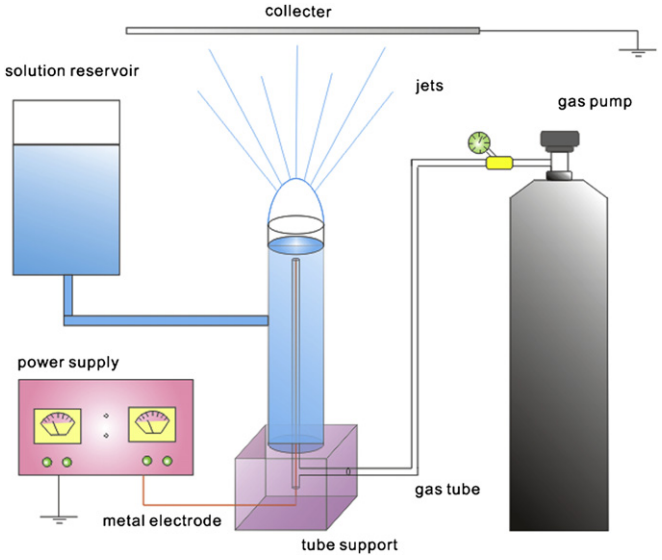

Fig. 3. Bubble-electrospinning experimental set-up. This principle to prepare for micro/nano fibers was patented (CHN Patent No. 200710036447.4). To use the principle to prepare for micro/nano products, transfer agreement must be made.

The morphology of the bubble-electrospun nanofibers were observed with a Field Emission Scanning Electron Microscope (Hitachi S-4800, Tokyo, Japan), see Fig. 4. The fiber dimensions were measured using Image J software. The diameter of an electrospun fiber usually varies along the fiber axis. The given FESEM illustrations reflect a very small part of the obtained fibers, so it is possible that the sample is from the same fiber.

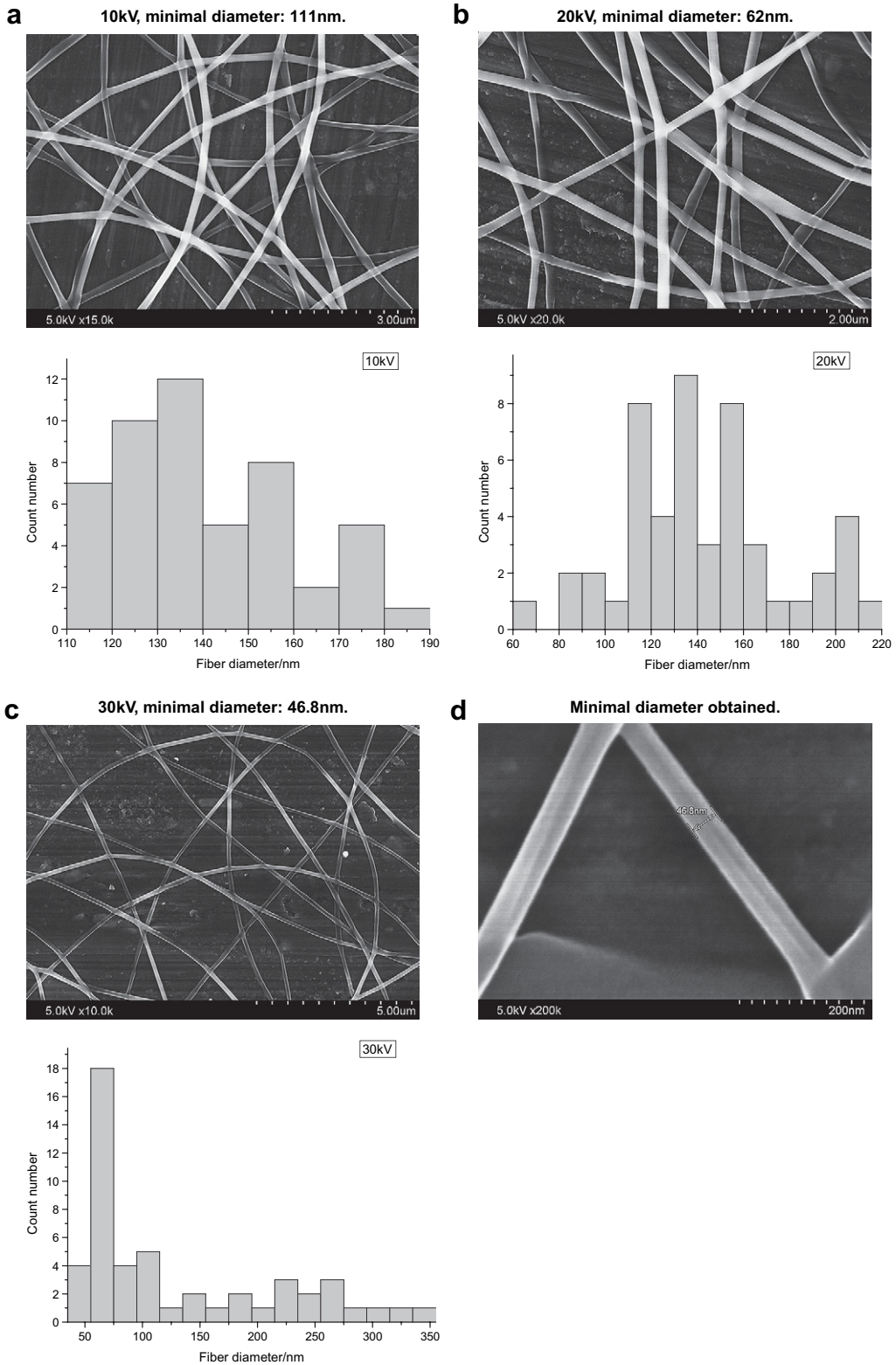

Fig. 4. Field emission scanning electron micrographs of bubble-electrospun nanofibers and fiber diameter size distribution. Applied voltages are, respectively, (a) 10 kV, (b) 20 kV, (c) 30 kV. The distance between the nozzle and the collector is adjusted to 8 cm. (a) 10 kV, minimal diameter: 111 nm. (b) 20 kV, minimal diameter: 62 nm. (c) 30 kV, minimal diameter: 46.8 nm. (d) Minimal diameter obtained.

4. Effect of applied voltage on fiber diameter

The applied voltage is the main force pulling the bubble into jets, we gave hereby a simple analysis of the effect of voltage on diameters of the fibers using scaling laws [24,25,26].

According to the Navier–Stokes equation for one dimensional charged jet, we have

$$u\frac{du}{dz} \propto F_E \tag{4}$$

where F_E is electric force applied on a single charged jet, u the velocity of the jet. We approximately assume that electric force depends linearly on the applied voltage:

$$F_E = a(V - V_0) \tag{5}$$

where V_0 is the threshold voltage, a is a constant.

Integrating Eq. (4) with respect to z, we have

$$\frac{1}{2}u^2 = az(V - V_0) + b \tag{6}$$

where b is an integrate constant. When $z = 0$ (see Fig. 2), the jet begins to eject, $u \approx 0$, so we have $b = 0$.

According to the conservation of mass, we have

$$\frac{1}{4}\pi d^2 \rho u = Q, \tag{7}$$

where Q is the mass flow rate, ρ is density, d the diameter of the charged jet.

Substituting Eq. (7) into Eq. (5), we obtain the following relationship

$$d = [\alpha(V - V_0)]^{-1/4} \tag{8}$$

where α is a constant.

Eq. (8) predicts that higher voltage results in smaller diameter of the fiber as illustrated in Fig. 4. In our experiment, the minimal diameter arrives at as small as 46.8 nm, shown in Fig. 4(d). The minimal diameter hereby refers to the one with minimal diameter in FESEM illustrations.

5. Discussion and conclusions

In this present work we focus ourselves on research into the effect of voltage on the diameters of the obtained nanofibers. In our experiment, only a single bubble is used, the diameter is about 11.5 mm, the static electric force acting on the bubble can be written in the form

$$F_E = \pi DT\delta \cos\theta - \frac{1}{4}\pi D^2(P_i - P_o) \tag{9}$$

Contrary to nano-bubbles in spider-spinning, a large bubble with diameter of 11.5 mm is created, this requires a high voltage to overcome the surface tension of the bubble. We apply high voltage in the bubble-electrospinning process in order to obtain a high acceleration of the charged jet, so that a high velocity can be reached. According to the mass conversation, Eq. (7), we can easily fabricate nanofibers under high voltage.

Water is selected as a solvent in our experiment. Important effect of solvent evaporation on the diameters was demonstrated in Ref. [27], and we will discuss the effect hereof.

Only a single bubble is studied in our work. The bubble's surface tension does not depend upon the fluid property, while the integrated force from surface tension that attaches the bubble to its support tube depends not only tube's diameter (bubble's size), but also the fluid property (viscosity).

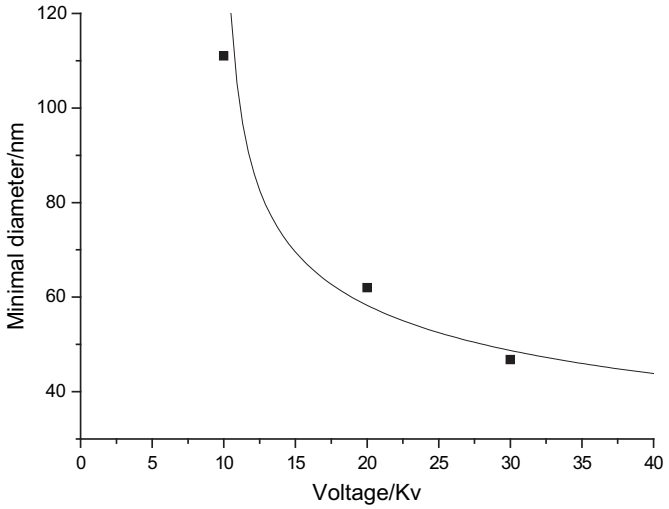

Fig. 5. Minimal diameter of nanofibers v.s. applied voltage. Dot: experimental, continuous line: theoretical prediction $d = [9 \times 10^{-9}(V - 9.9)]^{-1/4}$.

In this paper, water is used as solvent, which is widely adopted in environmentally benign manufacturing. The effect of voltage is investigated: when voltage is too low ($V < V_0$), it becomes inelectrospinnable. Fibers with smaller diameters are obtained for larger voltage as illustrated in Fig. 5. The minimal diameter reaches as small as 46.8 nm.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.10.021.

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