Single Polymeric Bubble for the Preparation of Multiple Micro/Nano Fibers

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ABSTRACT: Bubble-electrospinning is suggested to produce micro/nano fibers. Contrary to classical electrospinning where a high voltage is applied to overcome the surface tension of the Taylor's cone, in bubble-electrospinning, the voltage is applied to overcome the bubble's surface tension, which mainly depends upon the size of the bubble. Instead of single jet, millions of charged jets are observed simultaneously. In this article, we design a single bubble-electrospinning to primarily study the effect of concentration on the spinning procedure. Polyvinylpyrrolidone (PVP) is used in the experiment. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1161–1165, 2011

Key words: electrospinning; Taylor cone; bubble; nano/micro fibers; polyvinylpyrrolidone (PVP)

INTRODUCTION

Bubble-electrospinning was invented in 2007 (Ref. 1) and was further developed in 2008 (Ref. 2). It uses polymeric bubbles to produces millions of charged jets by applying a high voltage on the bubbles' surfaces to overcome the surface tension, various experiment showed that the output of fibers using bubble-electrospinning was greatly increased,[3–9] and the technology is suitable for mass production of micro/nano fibers.

The surface tension of a bubble does not depend upon solution properties but its size.[3,7,10] Contrary to classical electrospinning,[11–15] where high electric field is applied to a droplet of the polymer solution (Taylor cone), in the bubble-electrospinning, high electric field is applied to polymeric bubbles to overcome the surface tension of bubbles to produce millions of charged jets. Consider a bubble made by a polymer solution, and assume that the air pressures inside and outside the bubble are respectively P_i and P_0, its radius is r. The surface tension of the bubble, T, can be expressed as[4,6]

$$T = \frac{1}{2} r (P_i - P_0) \tag{1}$$

In case the bubble size tends to nano scales, the surface tension becomes extremely small, and it is easy to pull the nanobubbles into nanofibers as the case in spider-spinning system.[16] This technology was demonstrated to produce nanofibers as small as 50 nm.[4,9]

EXPERIMENTAL SECTION

Instrument

The system arrangement for single bubble-electrospinning is shown in Figure 1. In the center of the figure is a plexiglass tube filled of polymer solution by a thin plastic pipe, which connects the tube with the solution reservoir. In the tube a coaxial glass pipe is set from the bottom and the top of the glass pipe should be below the solution surface. Pumped gas (for example, air, N_2, CO_2, or inert gasses) flows through the inner glass pipe to produce continually a single bubble, which is used to fabricate micro/nano fibers, on the polymer solution surface. On the top of the tube only one bubble can be produced due to the restriction of the edge of the tube. The maximal diameter of the produced bubble is almost equal to the inner diameter of the tube, so the bubble size can be controlled by the tube diameter, whereas the diameter of the gas pipe hardly affects the bubble size. In our study, the inner diameter of the tube is fixed to be 12

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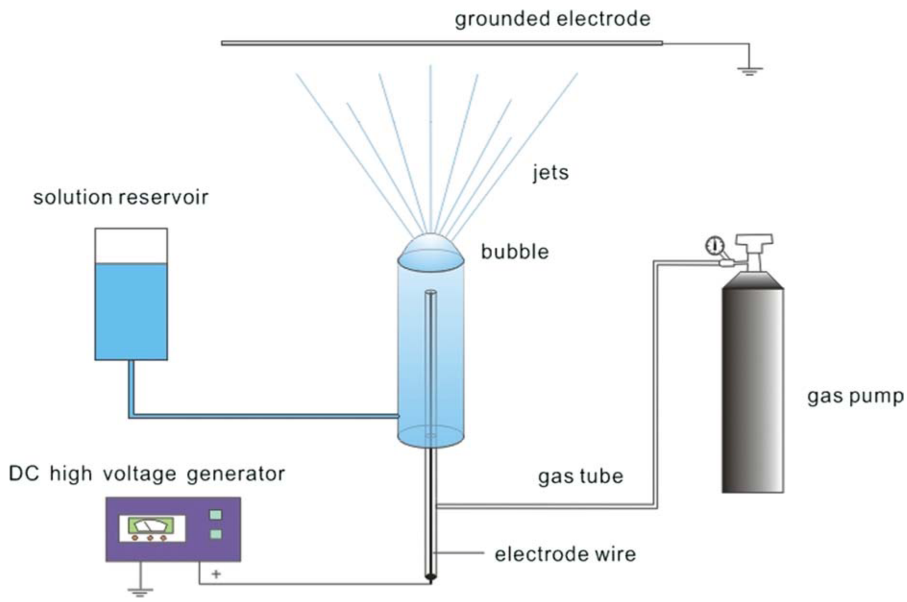

Figure 1 Single polymeric bubble for producing multiple jets. This principle to prepare for nano/micro products was patented (CHN Patent No. 200710036,447.4). To use this principle to prepare for micro/nano products, transfer agreement must be made. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mm. An electrically conductive wire, which acts as the positive electrode, is inserted into glass gas pipe. A high DC voltage generator is added to the conductive wire to produce a high electrostatic field near the bubble surface, a collected plate is placed over the tube, which serves as the grounded electrode. At a voltage sufficient to overcome surface tension of the produced bubble, charged fine jets of liquid shoot out and then are stretched and solidify in micro/nano fibers on the grounded electrode. The system arrangement of bubble-electrospinning can yield millions of polymer jets simultaneously with process controllability.

Materials

Polyvinylpyrrolidone (PVP), TritonR X-100, and absolute alcohol were purchased from Shanghai Chemical Reagent Co., China. Deionized water was supplied by the College of Chemistry, Donghua University.

Electrospinning process

To produce micro/nano fibers using the present experiment set-up, we used Polyvinylpyrrolidone (PVP-K30) with average molecular weight 40,000 g/mol. The applied voltage was 35 kV, the distance from the top of the tube to the grounded electrode was 18 cm and relative humidity was 52%. The prepared solutions were magnetically stirred at 28°C (environment temperature). Two different solvents were used in our experiment, all concentration measurements were done by weight (w/w).

Process I

Absolute alcohol was used as solvent. PVP with concentrations of 20, 25, 30, 35, and 40 wt % was dissolved in the solvent. TritonR X-100 was added into the solution at ratio 3 wt % as surfactant.

Process II

A mixture of deionized water and absolute alcohol with a weight ratio 1 : 9 was used as solvent. PVP with concentrations of 26, 30, 33, 36, and 40 wt % was dissolved in the solvent.

Morphology of fibers

The morphology of the electrospun PVP fibers by Process I was investigated using SEM. The SEM micrographs are shown in Figure 2. When the concentration was below a threshold value, no continuous fibers were produced except beads as shown in Figure 2(a). The explanation of this phenomenon was given in Ref. 14; when the concentration increased gradually, continuous fibers were observed as shown in Figure 2(b), where we could still find beads embedding on the fibers; the beads were deduced gradually with the increase of the polymer concentration and were disappeared completely when the concentration arrived at 35%. The minimal size of the obtained fibers was about 100 nm.

The SEM micrographs of Process II were shown in Figure 3. Similar phenomena were observed as those in Process I.

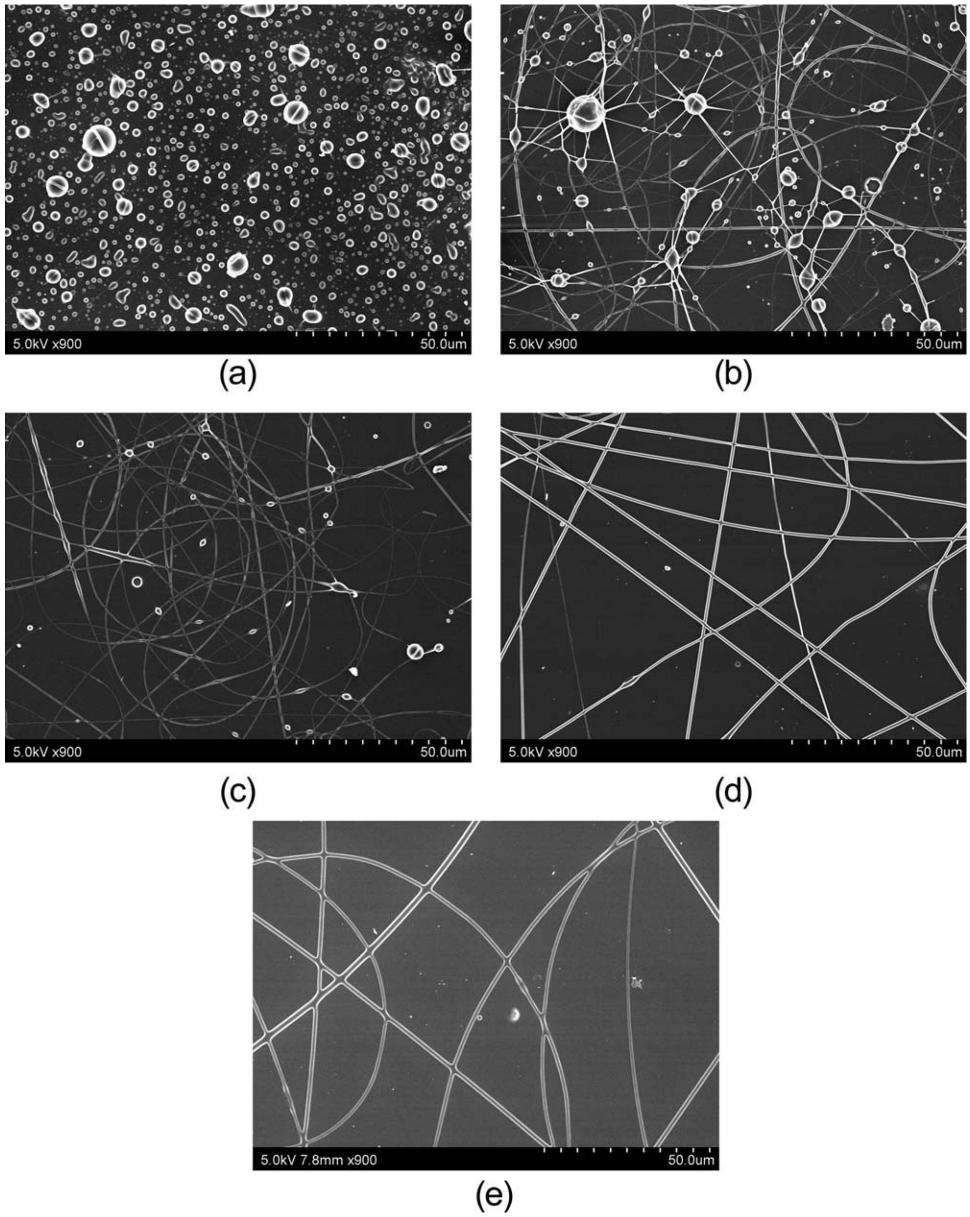

Figure 2 SEM micrographs of electrospun fibers produced in Process I. The concentrations (wt %) of PVP dissolved in absolute alcohol were (a) 20%, (b) 25%, (c) 30%, (d) 35%, and (e) 40%, and TritonR X-100 was added into the solution at ratio 3% as surfactant. The DC voltage connected to the positive electrode was 35 kV. The distance from the nozzles to the grounded electrode was 18 cm. The electrospinning process was carried out at temperature 28°C and relative humidity 52%.

EFFECT OF CONCENTRATION ON FIBER DIAMETER

Concentration of the electrospun polymer solution greatly affects spinningability. Generally solvents such as alcohol used in this study are small molecules, which can not be spun into fibers; macromolecules can be spun into fibers under suitable concentrations. When the concentration of the spun polymer solution is too low (the concentration of the solvent is too high), it becomes inspinningability as shown in Figure 2(a).

The governing equations for a charged jet are:[12,17,18]

1) The conservation of mass

$$\pi r^2 \rho u = Q, \tag{2}$$

where Q is the mass flow rate, ρ is density, r the radius of the charged jet, u the velocity of the jet.

2) The Navier-Stokes equation

$$u\frac{du}{dz} = F_E - g + \frac{d}{dz}\left(\mu\frac{du}{dz}\right) \tag{3}$$

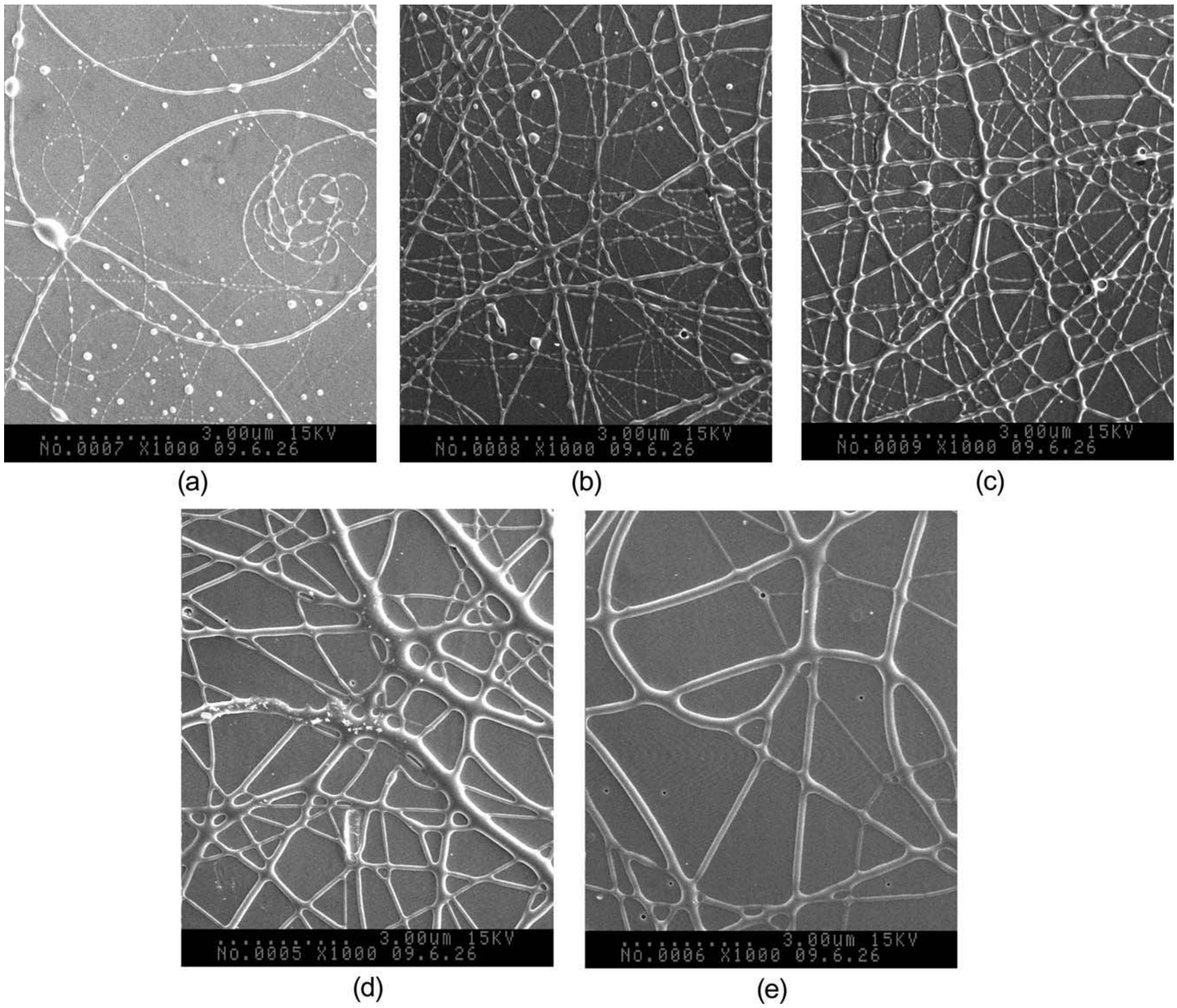

Figure 3 SEM micrographs of electrospun fibers produced in Process II. Deionized water and absolute alcohol was mixed with a weight ratio 1 : 9 as solvent. The PVP concentrations (wt %) were (a) 26%, (b) 30%, (c) 33%, (d) 36%, and (e) 40%. The DC voltage connected to the positive electrode was 35 kV. The distance from the nozzles to the grounded electrode was 18cm. The electrospinning process was carried out at temperature 28°C, and relative humidity 52%.

where F_E is electric force due to the applied voltage applied on a single charge jet, g is gravitation acceleration, μ viscous coefficient.

Integrating eq. (3) with respect to z yields

$$\frac{1}{2}u^2 = z(F_E - g) + \mu\frac{du}{dz} + D \tag{4}$$

where D is an integral constant.

To quantitatively analyze the effect of concentration on spinning process, we assume that du/dz is positive constant, from eq. (4) and (2), we have approximately the following scaling relationship

$$\mu \propto u^2 \propto r^{-4} \tag{5}$$

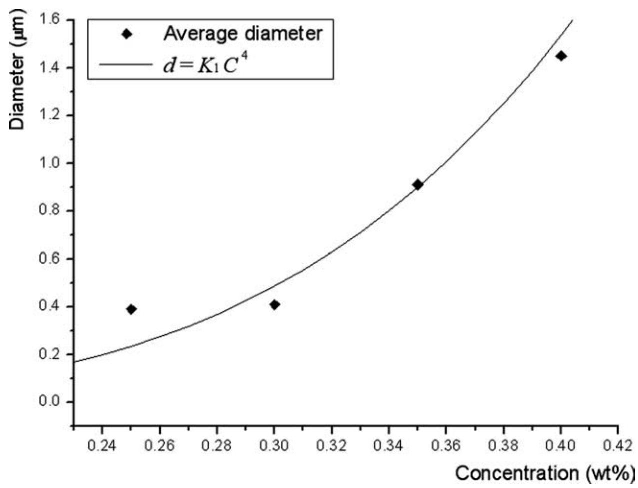

Figure 4 The relationship between the concentration and average diameter of the obtained fibers for the Process I. dot: average diameter, continuous line: theoretical prediction.

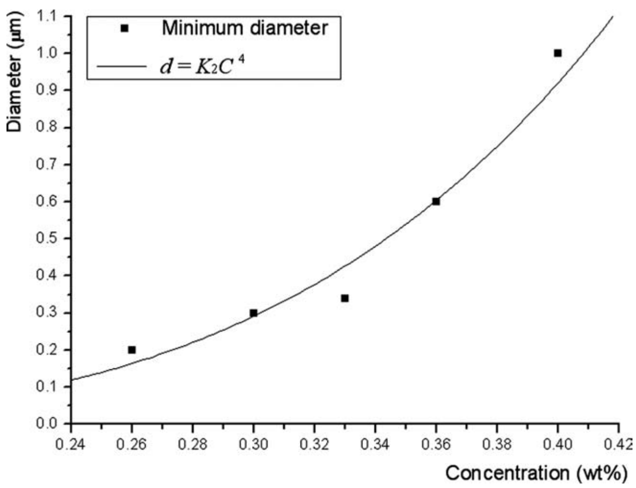

Figure 5 The relationship between the concentration and minimal diameter of the obtained fibers for the Process II. dot: minimal diameter, continuous line: theoretical prediction.

Viscous coefficient of the electrospun solution scales linearly with the polymer concentration, C:

$$\mu \propto C \tag{6}$$

From above eqs. (5) and (6), we can easily obtained the following approximate relationship

$$d = 2r \propto C^4 \tag{7}$$

where d can be the average diameter or the minimal diameter of the fibers.

Figure 4 shows the relationship between concentration and the average size of the obtained fibers for Process I, showing good agreement with our theoretical prediction. Figure 5 was the relationship between concentration and the minimal size of fibers observed in the SEM illustrations for Process II, also showing good agreement with our theoretical prediction. The present analysis is very crude, but the results are in good agreement with the experimental data as shown in Figures 4 and 5 and numerical results given in Ref. 19.

CONCLUSIONS

In this article, a single polymer bubble is used for preparing for micro/nano fibers, the effect of concentration is studied: when concentration is low, it becomes inelectrospinability, beads appear when concentration is near to the threshold value for inelectrospinability, this phenomenon is similar to that in classic electrospinning.[14] Fibers with larger diameter and bright and smooth surfaces are obtained for larger concentration as shown in Figures 2 and 3. The bubble-electrospinning is suitable for mass production of micro/nano fibers.

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