

FABRICATION OF NANOPOROUS FIBERS VIA BUBBLE ELECTROSPINNING

by

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A direct approach to fabrication of nanoporous fibers via bubble electrospinning is demonstrated. Solvent evaporation is a key factor for nanopore formation, and a theoretical model is established and analyzed. The paper elucidates a theoretical basis for the controllable preparation of nanoporous fibers.

Key words: bubble electrospinning, solvent evaporation, nanoporous fibers

Introduction

Recently, nanoporous fibers have been caught much attention as the most promising material in nanotechnology. To our knowledge, nanoporous materials have extremely high surface area and are widely used in different fields, such as filtration, radiation protection, catalysis, sensors, tissue engineering, and drug delivery [1-2]. Electrospinning is an effective method, which can fabricate polymer nanofibers and nanoporous fibers as well. The relatively high production rate, and simplicity of the setup make electrospinning very attractive to both academia and industry. He *et al.* produced nanoporous microspheres by electrospinning and established mathematical models for formation process [3, 4]. Some literature reported various fabrication processes for nanoporous materials [5, 6].

In this paper, nanofibers with nanopores on the surface are produced by bubble electrospinning of poly(lactic acid) (PLA) and 0.1% of nanosized Fe₃O₄ (particle size = 20 nm) mixed with CHCl₃(CF). The formation mechanisms of nanoporous fibers are discussed and researched. These nanoporous fibers may offer an alternative for new nanotechnology applications.

Solvent evaporation

Solvent evaporation in the electrospinning can results in the nanopores on the surface of nanofibers. The solvent decreasing from the jets allowed the charged jets to remain fluid and continue to stretch. Porous structure features on the fiber surfaces have been observed. It has been reported that highly volatile solvent could easily create nanopores on the fiber surfaces [7].

Formation of nanoporous fibers

Due to the instability of bubble electrospinning process, the formed nanofibers with nanopores have larger diameter, compared to the smaller nanofibers with smooth surfaces, as shown in fig. 1.

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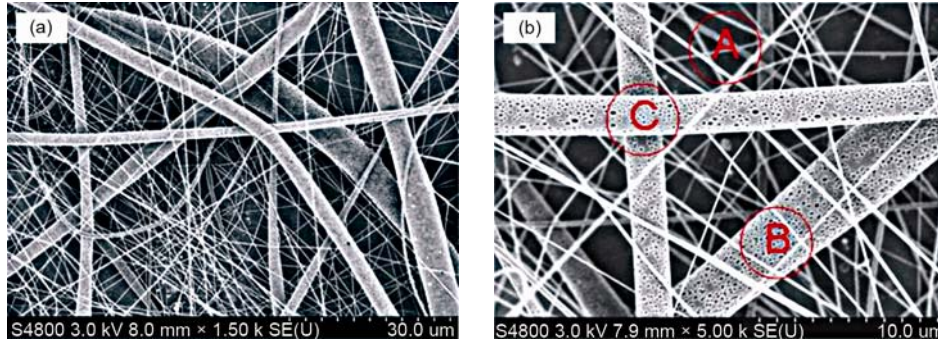


Figure 1. SEM photographs of bubble electrospun nanofibers with porosity

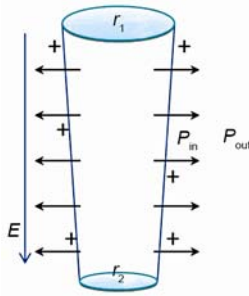


Figure 2. The schematic of solvent evaporation on the surface of the charged jets

Theoretical analysis

Using Darcy's law, we have:

$$V = k \nabla P = k \frac{P_{in} - P_{out}}{\Delta n} \quad (1)$$

where V is the rate of solvent evaporation, n – the radial scale, k – a constant, P_{in} and P_{out} are the surface pressure and outer pressure of the charged jet, respectively (fig. 2).

Pressure gradient is:

$$\frac{\partial P}{\partial n} = k \frac{P_{in} - P_{out}}{\Delta n} \quad (2)$$

When $\partial P / \partial n > \bar{Q}_c$, where $\bar{Q}_c$ is the critical value, solvents and small molecules from the jet surface evaporate.

During the bubble electrospinning process, the viscous jet is pulled from bubble surface and become much thinner under the electric force. The jet velocity is very high. Based on Bernoulli's equation, which reads:

$$\frac{1}{2} u^2 + \frac{P}{\rho} = B \quad (3)$$

where u is the jet velocity, P – the fluid pressure, and ρ and B are constants for the incompressible fluid.

Based on eqs. (2) and (3), eq. (1) can be transformed:

$$V = k \nabla P = \tilde{k} [P(R) - P_{out}] = \tilde{k} \left(B \rho - \frac{1}{2} \rho u^2 - P_{out} \right) = a - b u^2 \quad (4)$$

where R is the surface radius of the jet and a and b are constants.

The radial velocity distribution of the charged jet is expressed as:

$$u = c + dr^2 \quad (5)$$

By eqs. (3) and (4), the evaporation rate can be concluded, which reads:

$$V = k \nabla P = k \left. \frac{dP}{dr} \right|_{r=R} \quad (6)$$

According to eqs. (5) and (6), thus further the evaporation rate is expressed as:

$$V = -k\rho u \left. \frac{du}{dr} \right|_{r=R} \quad (7)$$

Although 1-D model for bubble electrospinning process is simple and mathematically tractable, theoretical analysis shows that the electric force acts only on the surface of the charged jets, resulting in a nonuniform velocity distribution on the section of a jet, a mathematical model for the velocity distribution is, therefore, much needed. The theoretical analysis reveals that temperature of the jet can greatly affect the velocity distribution.

Combining eqs. (5) and (7):

$$V = 2kd\rho(c + dR^2)R \quad (8)$$

Solvent evaporation rate is proportional to the radius of the jet, namely the thicker the jet, the easier solvent evaporation.

We refer to the following mass conservation equation:

$$Q = \int_0^R 2\pi r \rho u \, dr \quad (9)$$

Equation (5) is merged into eq. (9), which reads:

$$Q = \pi\rho \left(c + \frac{1}{2} dR^2 \right) R^2 \quad (10)$$

The smaller flow results in the thicker jet, and the solvent on the surface of the jet is much easier to evaporate. So many nanopores form on the surface of solidified fibers. Conversely, it is difficult to form nanopores on the thinner fiber surfaces. During the process of spinning, solvent evaporation on the fiber surface is controlled by regulating the flow of solution, eventually achieving controllable morphology for the nanofibers.

During the bubble electrospinning process, the jets are drawn under the action of electric field force and surface solvent evaporates before solidification. The surface pressure reach a certain critical value P_{cr} at the moment of t_1 . Meanwhile, the surface solvent evaporation is less, the jets continue to stretch and eventually form uniform and smooth nanofibers (fig. 3a). At the same time, if the pressure $P_{cr} + \varepsilon$ on the surface of the jets is larger than the critical value, the surface solvent evaporated heavily. According to conservation of energy, the jets do not have enough energy to be stretch, which results in the thicker fiber diameter. Finally, the porous phenomenon appears on the surface (fig. 3b). In addition, if the surface pressure is equal to the critical value, the solvent evapora-

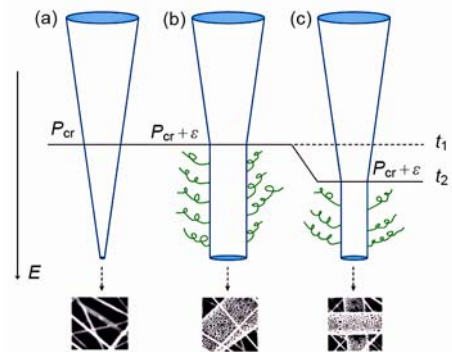


Figure 3. The formation mechanisms of bubble-electrospinning nanoporous fibers. (a), (b), and (c) represent three different solvent evaporation in the process of the jet movement, respectively. At the bottom are corresponding SEM photos

tion is less. But at the moment of t_2 ($> t_1$), the pressure $P_{cr} + \varepsilon$ on the surface of the jets is larger than the critical value and subsequently the surface solvent has a large amount of evaporation. Similarly, nanoporous fibers with thinner diameter than that of fibers (fig. 3b) are formed (fig. 3c).

Conclusions

A novel strategy for fabrication of continuous nanoporous fibers by bubble electrospinning is presented. The results obtained by applying the mathematical models are in good accordance with the experimental data. Nanopores uniformly distributes on the surface of nanofibers with larger diameters. These nanoporous materials maybe will achieve a new breakthrough in the fields of applications.

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