A MATHEMATICAL MODEL FOR THE FORMATION OF BEADED FIBERS IN ELECTROSPINNING

by

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Beaded fibers are often observed in electrospinning. However, its formation mechanism is not well understood. A mathematical model for pulsation of the charged jets during spinning is proposed to reveal the phenomenon of beaded fibers, and the main factors for beaded fibers are elucidated.

Key words: *beads, electrospinning, analytical solution, silk*

Introduction

In recent years, the electrospinning process has aroused great interest as a convenient and attractive technique for fabricating macro/nanofibers, however, beaded fibers are frequently formed in electrospinning [1].

Various experiment [2, 3] revealed that the formation of a beaded fiber was mainly due to changes in some spinning parameters, such as solution concentration, applied voltage, solution surface tension, and conductivity. It is found experimentally that the solution concentration is the straightforward and key factor among all factors [1]. The beaded fibers are related to the instability of the jet of polymer solution, as revealed by Entov *et al*. [4], who established mathematical models to describe breakup of jets of polymer liquids. Shin *et al.* [5] established a mathematical model for spinning process of electrospinning. He and Kong [6] established a criterion for an oscillatory charged jet during the bubble spinning process. Although these studies and theoretical models are helpful to understand the spinning process, the theoretical insight into the beaded fibers is rare and preliminary [1, 6]. Herein, a pulsation model is put forward to reveal the phenomenon.

Modeling and experimental verification

Figure 1 shows the electrospinning process, and we consider an infinitesimal volume with length of Δz to establish a mathematical model for electrospinning. The volume of infinitesimal volume is $\pi r^2 \Delta z$, the total surface charge is $2\pi r \Delta z \sigma$, where r is the radius of the jet

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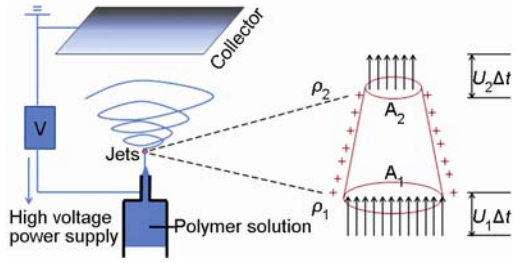

Figure 1. Proposed charged jets in electrospinning

at axial co-ordinate z, ρ – the liquid density, τ – the viscous force, σ – the unit charge density on the surface, E – the applied electric field, and u – the velocity.

The momentum equation for 1-D flow is:

$$\rho\pi r^2\Delta z\frac{Du}{Dt}=2\pi r\Delta z\sigma E+\pi r^2\Delta z\frac{\partial\tau}{\partial z} \tag{1}$$

The flow is assumed to be Newtonian one, and the viscous force can be expressed as:

$$\tau=\mu\frac{\partial u}{\partial z} \tag{2}$$

where μ is the viscosity coefficient.

For steady jets, in view of eq. (2), eq. (1) can be simplified as:

$$u\frac{\partial u}{\partial z}=\frac{2\sigma E}{\rho r}+\frac{\mu}{\rho}\frac{\partial^2 u}{\partial z^2} \tag{3}$$

(1) Charge balance equation

$$2r\sigma u+r^2kE=I \tag{4}$$

where k is the conductivity of the fluid.

In view of eq. (4), we can re-write eq. (3) in the form:

$$u\frac{\partial u}{\partial z}=\frac{E(I-r^2kE)}{\rho r^2u}+\frac{u}{\rho}\frac{\partial^2 u}{\partial z^2} \tag{5}$$

(2) Conservation of mass equation

The mass equation for 1-D steady jet can be written in the form:

$$\rho ur^2=Q \tag{6}$$

where Q is a constant.

By the mass equation, we can simplify eq. (5):

$$\frac{\partial^2 u}{\partial z^2}-au\frac{\partial u}{\partial z}-\frac{b}{u}+c=0 \tag{7}$$

Introducing a new variable v, defined as $v=u-\beta$, we can convert eq. (7) to the form:

$$\beta\frac{\partial^2 v}{\partial z^2}+cv+v\frac{\partial^2 v}{\partial z^2}-av^2\frac{\partial v}{\partial z}-a\beta^2\frac{\partial v}{\partial z}-2av\beta\frac{\partial v}{\partial z}+c\beta-b=0 \tag{8}$$

Setting the $c\beta-b=0$, we have:

$$\frac{\partial^2 v}{\partial z^2} + \omega^2 v + \frac{1}{\beta}\left(v\frac{\partial^2 v}{\partial z^2} - av^2\frac{\partial v}{\partial z} - a\beta^2\frac{\partial v}{\partial z} - 2av\beta\frac{\partial v}{\partial z}\right) = 0 \tag{9}$$

where

$$\omega^2 = \frac{c}{\beta} = \frac{I^2\rho^2}{k\mu Q^2} = \frac{(EI)^2\rho^2}{k\mu Q^2 E^2}$$

In the electrospinning process, electronic energy *IE* keeps unchanged, while the current is almost zero, that is $I \ll 1$, as a result we have the following zero-order approximate periodic solution:

$$v = A\cos(\omega z + \theta_0) \tag{10}$$

where

$$\omega = \frac{(EI)\rho}{EQ}\sqrt{\frac{1}{k\mu}} \tag{11}$$

where the *IE*, ρ, and Q are constants.

From eq. (11), we know that the frequency of the jets is inversely proportional to the polymer viscosity coefficient. To further expound this pulsation model, the mechanism of structure transition with the increase of polymer concentration and polymer viscosity was assumed in fig. 2.

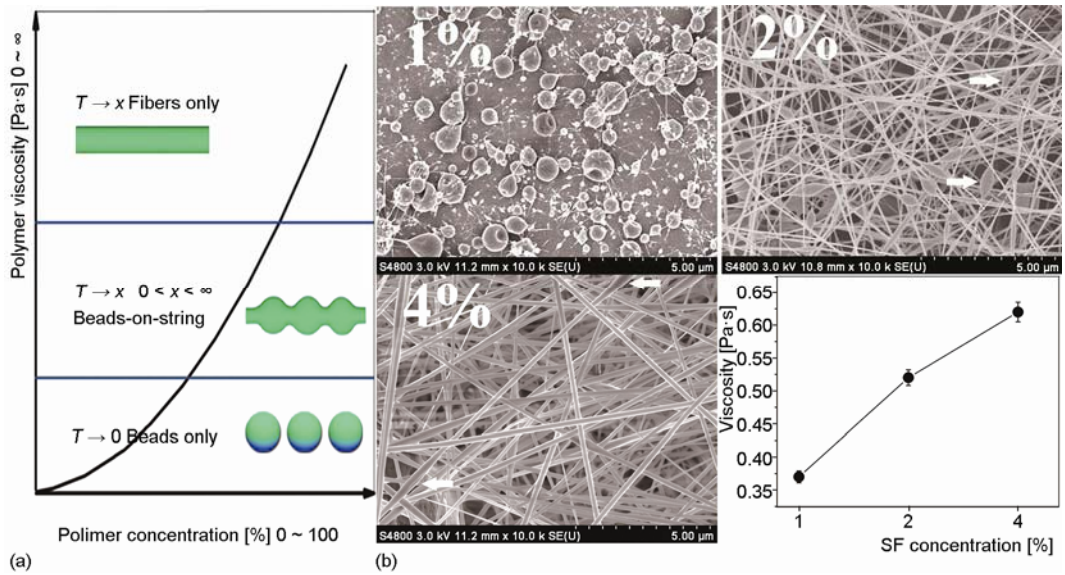

Figure 2. Mechanism of beaded fibers; (a) pulsation period, (b) SEM illustrations of silk fibroin (SF) nanofibers prepared with solution concentrations of 1%, 2%, and 4%, respectively

As shown in fig. 2(a), when the jet reaches a threshold, instability of the jet occurs and three situations are predicted. One is that at low polymer concentration (when the value is zero). From eq. (11), we get a zero of T ($\omega \to \infty$). In this situation, pulsation frequency is so high that the jet appears to be splitting into multiple filaments, and additional types of insta-

bilities may lead to breakup of the jet into droplets [7]. As a result, beads only are obtained, fig. 2(a). Another is the opposite situation. When polymer concentration tends to infinity, we have that T tends to infinity ($\omega \to 0$), which means that the pulsation of the jet is not happened. Therefore, smooth fibers without beads can be obtained, fig. 2(a). Meanwhile, the morphological transition from bead dominant to fiber dominant structure took place gradually over a rage of SF concentrations and viscosities from 1% to 4% and with the distance between beads increase obviously, fig. 2(b). Plenty of beads were observed and they aggregated together (when 1% SF concentration). When 2% SF concentration, beaded fibers were obtained, and the distance between two adjacent beads is about 1.6 μm to 7.0 μm, fig. 2(b). Interestingly, the distance between two adjacent beads become longer to more than 10.0 μm, fig. 2(b) (when 4% SF concentration). In reality, it was difficult to see beads any more, which is well accordance with model proposed.

Conclusions

In summary, SF nanofibers were prepared by electrospinning, and the experimental observations are in good agreement with the model which associated the pulsation of the electrospinning jets with the polymer viscosity and concentration. The concise, accompany with effective makes this pulsation model have profound guiding significance for fabricating and applications of macro/nanofibers.

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