MECHANISM OF NANOFIBER CRIMP

by

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Fabrication of crimped fibers has been caught much attention recently due to remarkable improvement surface-to-volume ratio. The precise mechanism of the fiber crimp is, however, rare and preliminary. This paper finds that pulsation of fibers is the key factor for fiber crimp, and its configuration (wave formation) corresponds to its nature frequency after solidification. Crimping performance can be improved by temperature control of the uncrimped fibers. In the paper, polylactide/dimethylfomamide solution is fabricated into crimped nanofibers by the bubble electrospinning, an approximate period- amplitude relationship of the wave formation is obtained.

Key words: *crimp, nanofibers, bubble electrospinning, nature frequency, thin plate, nonlinear vibration*

Introduction

Crimp characteristic of fibers is one of the most essential parameters to influence processing performance and product quality [1-4]. Common crimping and texturing procedures mainly include the false twist texturing, the stuffer box texturing, the impacting texturing, the edge crimping, the gear crimping, the knit-deknit, the air-jet texturing and the bicomponent crimping [5-9], a complete review on various fiber crimp is available in ref. [4]. These traditional technologies of fiber crimp are mature for mass-production of crimped fibers, however, the precise mechanism of the fiber crimp is rare and preliminary, and those technologies cannot be used for fabrication of crimped nanofibers, which have remarkable surface-to-volume ratio, and have many potential applications in various applications, such as wound dressing, filtration application, tissue engineering, drug delivery, catalyst supports, biotechnology, medical treatment, military security, environment, textile and other industries [10].

This paper begins with the stuffer box crimping and its crimp mechanism, which is then further extended to fabricate crimped nanofibers by the bubble electrospinning [10-12].

Stuffer box crimping

The stuffer box crimping is a widely used method for fabrication of crimped fibers [4]. Figure 1 reveals the process of crimp formation. Heated and softened fibers are fed into a chamber until they meet the wall of the upper doctor blade, which hinders the motion of fibers and acts a normal force on the fibers. A long fiber becomes instable due to the disturbance of the normal force (fig. 2), and it pulsates (that is, the fiber oscillates in size) at its natural frequency, and its wave-like configuration corresponds to its nature frequency. It is necessary

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that the fiber is solidified when the pulsation occurs, so it is important to control the temperature in the stuffer box, because temperature can greatly affect the flexural rigidity of the fiber.

In this paper we will extend the pulsation mechanism of fiber crimp into fabrication of crimped nanofibers by the bubble electrospinning.

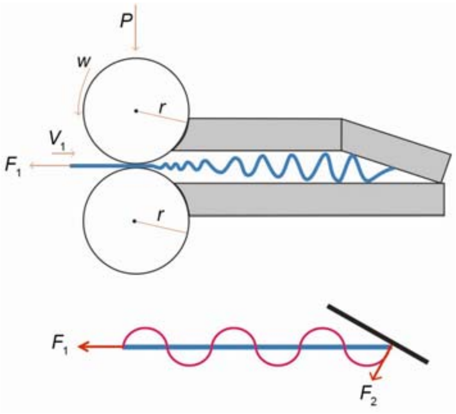


Figure 1. Crimping mechanism in the stuffer box

Nanofiber crimp

The bubble electrospinning is a promising technology for mass-production of various nanomaterials [10-12]. Hereby we show that it can be used for fabrication of crimped nanofibers. When a bubble is ruptured in the bubble electrospinning process, multiple jets are formed and accelerated by the electronic force. Nanofiber crimp occurs when the moving jet arrives at the receptor (fig. 2). The receptor serves the same role as the upper doctor blade in the stuffer box crimping. The nano/micro jet during the spinning process is extremely instable, when a normal force by the receptor acts on the frontier of the jet, which is not solidified completely yet, pulsation occurs, and wave-like formation is formed after complete solidification.

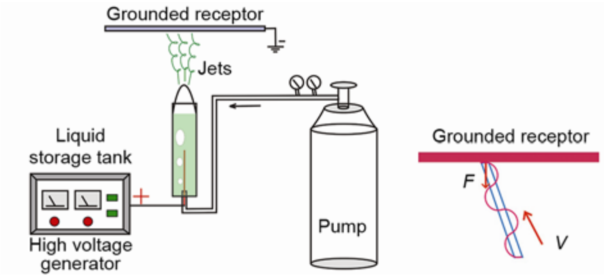


Figure 2. Crimping mechanism in the bubble--electrospinning

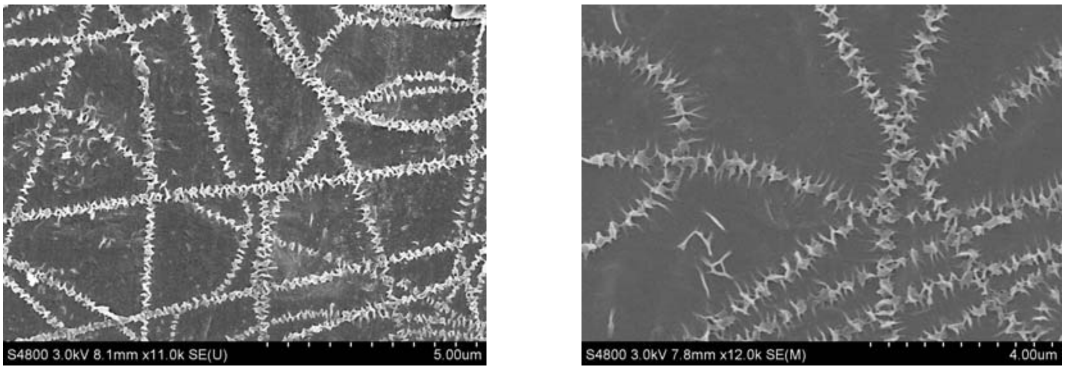
Experimental

Polylactide (PLA), with the molecular weight of $M_n \approx 80000$, and N,N-dimethylfomamide (DMF), with the molecular weight of $M_n \approx 73.09$, were used in the experiment. PLA particles were dissolved into DMF solution with the temperature 24.3 °C and the humidity 52%. The mixture was stirred with the aid of electromagnetic stirrer at 80 °C for two hours to get homogeneous and transparent solution and cooled to the room temperature before the experiment. The concentration of PLA was 10 wt.%.

The bubble-electrospinning set-up is illustrated in fig. 2. It contains a liquid storage tank, a high voltage generator, a pump, a grounded receptor, and electrodes. The grounded receptor was placed 20 cm upper to the liquid storage tank. The voltage applied was maintained at 20 kV. Samples were pasted on a scanning electron micro-scope (SEM) disk and coated with gold before being observed through SEM. The morphology of PLA/DMF nanofibers is illustrated in fig. 3.

As a preliminary study, we consider the charged jet in the spinning process as an elastic rod under constant thermal expansion, its transverse vibration can be expressed in the form [13]:

$$EI\frac{\partial^4 w}{\partial x^4} + N\frac{\partial^2 w}{\partial x^2} + \rho A\frac{\partial^2 w}{\partial t^2} = 0 \tag{1}$$



(a) (b)

Figure 3. Morphology of PLA/DMF nanofibers. The period and amplitude for (a) and (b) are 0.234 μm and 0.153 μm; 0.239 μm, and 0.247 μm, respectively

where A is the fiber's cross-sectional area, EI – the flexural rigidity, ρ – the density, and N – the thermal effect:

$$N = \alpha \Delta TEA - \frac{EA}{2L}\int_0^L \left(\frac{\partial^2 w}{\partial x^2}\right)^2 \mathrm{d}x \tag{2}$$

where α is the thermal expansion coefficient, and ΔT – the temperature change.

Assume that the transverse displacement can be expressed in the form:

$$w(x,t) = \left(1 - \cos\frac{2\pi x}{L}\right)u(t) \tag{3}$$

Substituting eq. (3) into eq. (1), after some simplification, we have:

$$\frac{\mathrm{d}^2 u}{\mathrm{d}t^2} + \omega_0^2 u + \varepsilon u^3 = 0 \tag{4}$$

where $$\omega_0^2 = \frac{4\pi^2}{3\rho a L^2}\left(\frac{4\pi^2 EI}{L^2} - \alpha \Delta TEA\right), \quad \varepsilon = \frac{4\pi^4 E}{3\rho L^4}$$

Equation (4) is the well-known Duffing equation, where the non-linear restoring force can be written in the form:

$$f(u) = \omega_0^2 u + \varepsilon u^3 \tag{5}$$

When u reaches its maximum, *i. e.*, $u = B$, where B is the amplitude, its restoring force becomes maximal, and we assume:

$$f(B) = kB \tag{4}$$

where k is an equivalent spring constant.

In case $\varepsilon = 0$, the square of its frequency can be easily obtained, which reads:

$$\omega^2 = \frac{f(B) - f(0)}{B} = \frac{\omega_0^2 B - 0}{B} = \omega_0^2 \tag{5}$$

For a non-linear restoring force, we can approximately obtain the square of its frequency, which is:

$$\omega^2 = \frac{f(B) - f(0)}{B} = \omega_0^2 + \varepsilon B^2 \tag{6}$$

This is less accurate, but the calculation is considerably shorter. To improve its accuracy, we re-write eq. (6) in the form:

$$\omega^2 = \frac{f(B) - f(0)}{B} \approx f'\left(\frac{B}{2}\right) \tag{7}$$

where $f'(B/2)$ is the slope at $u = B/2$.

By eq. (7), the square of its frequency can be immediately obtained, which reads:

$$\omega^2 = f'(u)\big|_{u=B/2} = \omega_0^2 + 3\varepsilon\left(\frac{B}{2}\right)^2 = \omega_0^2 + \frac{3}{4}\varepsilon B^2 \tag{8}$$

or

$$\omega = \sqrt{\omega_0^2 + \frac{3}{4}\varepsilon B^2} = \sqrt{\frac{4\pi^2}{3\rho a L^2}\left(\frac{4\pi^2 EI}{L^2} - \alpha\Delta TEA\right) + \frac{\pi^4 EB^2}{\rho L^4}} \tag{9}$$

The accuracy improves much, and it reaches 7% even when $\varepsilon \to \infty$. The transverse motion is therefore obtained, which reads:

$$w(x,t) = B\left(1 - \cos\frac{2\pi x}{L}\right)\cos\omega t \tag{10}$$

For all fixed spinning conditions, the period-amplitude relationship can be expressed as:

$$T = \frac{1}{\sqrt{a + bB^2}} \tag{11}$$

where a and b are constants. For the present experiment (fig. 2), we have:

$$T = \frac{1}{\sqrt{18.73 - 20.11B^2}} \tag{12}$$

Conclusions

Along with the remarkable improvement surface area, crimped nanofibers have been possessed plenty of excellent and fantastic properties such as unusual high surface energy, superior surface reactivity, radiation protection, admirable thermal and electric conductivity. It is necessary that the jet is not solidified completely when pulsation occurs.

Crimp fibers are of great influence on the processing performance of the fibers. This paper suggests that bubble electrospinning can be used to fabricate crimped nanofibers at one step.

Furthermore, we suggest an utmost simple method to determine the frequency of a non-linear oscillator, its accuracy is relatively acceptable, while the calculation is considerably easy, and accessible to all non-mathematicians.

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