SEA-SILK BASED NANOFIBERS AND THEIR DIAMETER PREDICTION

by

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Diameter of sea-silk based nanofibers prepared by electrospinning is closely related to the concentrations of sea-silk solution. A mathematical model is established according the mass conservation law in fluid mechanics to predict the diameter of fibers, and the MATLAB software is used to fit the experiment value. The results show that the fitted equation is quite accurate and efficient for estimating the diameter of fibers with different concentrations.

Key words: *electrospinning, sea-silk, mathematical model, nanofiber, fiber's diameter.*

Introduction

Electrospinning is an effective way to prepare nanofibers, it is a fabrication process that uses an electric field to control the deposition of polymer fibers onto a receptor [1-8]. In electrospinning process, the diameter of nanofiber is determined by many factors, like voltage, viscosity of solution, receptor's distance, environment temperature, environment humidity, *etc.* [9, 10]. Nanofiber's diameter and morphology can also be controlled by additives [11]. The sea silk is one of the oldest natural silks, which has a history of more than 5000 years [12-16], and now we can produce artificial sea silk through Mytilus edulis. To this end, we extract protein from Mytilus edulis and then use it as an additive for electrospinning, this maybe has some effects on the morphology of fibers. In this paper, we fabricate sea silk-based nanofibers with different concentrations of sea-silk solution, and determine the relationship between fibers' diameter and sea-silk's concentration.

Experiment

Polyvinyl alcohol (PVA) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and used as received. Alcoholysis degree of the PVA was 97.5-99.0 mol%.

Alive Mytilus edulis was purchased from Shensi Island, Zhoushan City, Zhejiang Province, China. We opened the Mytilus edulis' shell, and exploited the whole mussel meats, then mixed the mussel meats with alcohol, and the mixture was stirred until a homogeneous solution was obtained. The solution was filtered using a 500 mesh filter screen to obtain a sea silk solution.

The 4g PVA and 2 g sea-silk solution were mixed with 44 g deionized water, the mixture was magnetically stirred using a heating magnetic stirrer (DF-101S, Xinrui Instrument

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Table 1. Six samples with different concentrations of sea silk solution

Sample No. 1	PVA:sea-silk solution = 1:0
Sample No. 2	PVA:sea-silk solution = 2:1
Sample No. 3	PVA:sea-silk solution = 1:1
Sample No. 4	PVA:sea-silk solution = 1:2
Sample No. 5	PVA:sea-silk solution = 1:2.5
Sample No. 6	PVA:sea-silk solution = 1:3

Inc., Beijing, China) under the temperature of 80 °C until the PVA particles were completely dissolved into a homogeneous solution. Before spinning, the spun solution was stirred again on an ultrasonic cleaner (SL-5200DT, Nanjing Shunliu Instrument Co., Nanjing, China) for 2 hours to improve the dispersion of sea-silk solution in the spun solution. We prepared for 6 samples with 8 w.t% PVA and different concentrations of sea-silk solution, listed in tab. 1.

Fiber's morphology was analyzed using a S4800 cold field scanning electron microscope (SEM), by Hitachi S-4800, Tokyo, Japan, fiber's diameter distributions were analyzed with IMAGEJ software (National Institute of Mental Health, Bethesda, Maryland, USA).

Results and discussion

It is obvious that the concentration of the sea-silk solution can greatly affect fiber's diameter, tab. 2. This is because Mytilus edulis protein has a property of fast gelation. During electrospinning, when a jet is ejected from the Taylor cone, the proteins will be solidified immediately. When the proteins were solidified, the jet motion was hindered, resulting in a large fiber diameter. This can be explained by the mass conservation law in fluid mechanics. As the concentration of sea-silk solution increases, the protein concentration increases correspondingly, protein will be solidified at the initial stage of the spinning process, as a result, a higher solid-to-liquid ratio in the moving jet is predicted, and a larger fiber is produced, as the cases for Samples 2~6, see fig. 1.

Table 2. The average diameter for 6 samples

Different solution	Average diameter, D [nm]	Standard deviation, σ [nm]	Confidence interval [nm]
Sample 1	178	21.8	±4
Sample 2	200	27.9	±5
Sample 3	201	23.3	±5
Sample 4	278	35.9	±7
Sample 5	303	95.5	±18
Sample 6	331	109.8	±22

Considering a section of a moving jet during the spinning process, consisting of PVA solution and sea-silk solution, we have:

$$A = c_1 A_1 + c_2 A_2 \tag{1}$$

where A is the section area of the jet, A_1 and A_2 are the occupied areas of PVA solution and sea-silk solution, respectively, c_1 and c_2 are the concentrations of the PVA solution and sea-silk solution, respectively, they should also satisfy $c_1 + c_2 = 1$.

Due to the fast solidification of proteins in sea-silk solution, the solidified proteins occupy part of the section area, and the occupied area is directly proportional to the concentration of the sea-silk solution:

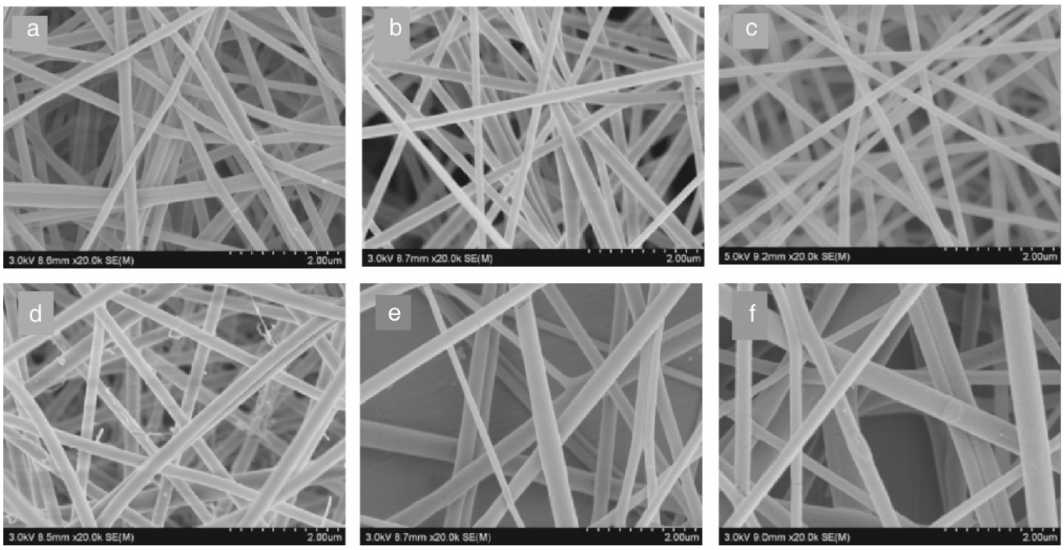

Figure 1. The SEM pictures of the nanofibers with different concentration, (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, (e) Sample 5, (f) Sample 6

$$\Delta S \propto c_2^{\alpha} \tag{2}$$

Assuming that the jet radius is r, we have:

$$r^2 - r_0^2 = \frac{\Delta S}{\pi} \propto c_2^{\alpha} \tag{3}$$

where r_0 is section radius for $c_2 = 0$ (Sample 1).

It means

$$r = \sqrt{r_0^2 + kc_2^{\alpha}} \tag{4}$$

where k is a constant.

We fit the experimental value through MATLAB software, when $\alpha = 1.618$, $r_0 = 135$, $k = 124230$, eq. (4) becomes:

$$r = \sqrt{135^2 + 124230 c_2^{1.618}} \tag{5}$$

The error between experiment value and theoretical prediction is small, see fig. 2.

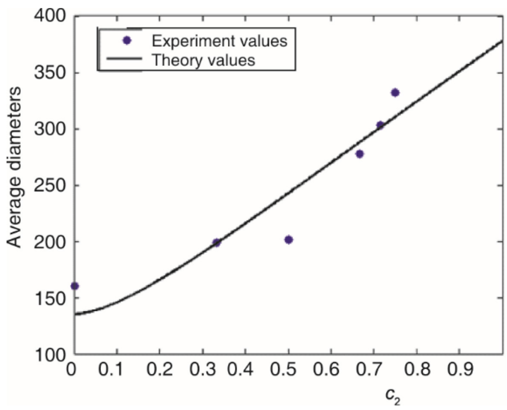

Figure 2. Experimental data *vs.* theoretical prediction

Conclusions and remarks

In this paper, we prepared sea silk-based nanofibers with different concentrations by electrospinning. The experiment results showed that the fiber's diameter is closely related to the concentrations of sea-silk solution. We used MATLAB to fit the experiment values, and found the relationship between the fibers' diameter and sea-silk's concentration. There leaves much space to further study the applications of the sea-silk-based nanofibers in future, Macromolecular electrospinning [17, 18] can be also used to study the property of the artificial sea silk from macromolecular level.

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