Non-ionic surfactants for enhancing electrospinnability and for the preparation of electrospun nanofibers

Shu-Qiang Wang
Ji-Huan He, Donghua University
Lan Xu
Non-ionic surfactants for enhancing electrospinability and for the preparation of electrospun nanofibers

Shu-Qiang Wang,1,2 Ji-Huan He1,3* and Lan Xu1,3

1Key Laboratory of Science & Technology of Eco-Textile, Donghua University, Ministry of Education, China
2College of Science, Donghua University, 1882 Yan-an Xilu Road, Shanghai 200051, China
3Modern Textile Institute, Donghua University, 1882 Yan-an Xilu Road, Shanghai 200051, China

Abstract

BACKGROUND: Electrospinning is widely used to produce nanofibers; however, not every polymer can be electrospun into nanofibers. To enhance electrospinability, much effort has been made in designing new apparatus, such as vibration-electrospinning, magneto-electrospinning and bubble-electrospinning.

RESULTS: A representative non-ionic surfactant, TritonX-100, is used to enhance electrospinability. The surfactant is added to an electrospun poly(vinyl pyrrolidone) polymer solution, and a dramatic reduction in surface tension is observed. As a result, a moderate voltage is needed to produce fine nanofibers, which are commonly observed during the conventional electrospinning procedure only at elevated voltage.

CONCLUSION: The novel strategy produces smaller nanofibers than those obtained without surfactants, and the minimum threshold voltage is much decreased.

© 2008 Society of Chemical Industry

Keywords: electrospinning; surfactant; PVP; nanofibers

INTRODUCTION

Electrospinning is a simple, versatile and powerful approach to producing nanofibers from various synthetic and natural polymers.1–5 Nanofibers sometimes behave extremely well in many respects due to nano-effects,6–8 for example remarkable strength, high surface energy and surface reactivity, and excellent thermal and electric conductivity, and serve as promising materials in nanotechnology and a highly versatile platform for a broad range of applications in widely different areas such as photonic structures, microfluidic channels (nanofluidics), catalysis, sensors, medicine, environmental engineering, defense and security, energy storage, invisibility devices (e.g. stealth aircraft and clothing) and radioprotection, to name just a few. Recent studies on the nanostructure of goose down showed both the excellent thermal insulation and breathability of goose down.9,10

The last decade of electrospinning technology has seen a sharp rise in fabrication and application of nanofibers.11–20 However, not every polymer can be prepared for electrospinning. Generally speaking solutions of polymers with too low or too high a molecular weight cannot be electrospun into continuous fibers. Electrospinnability mainly depends upon the solution viscosity,21 and vibration-electrospinning21–24 was designed to enhance electrospinnability markedly even for very high viscosity.22 In the work reported in this paper we used a non-ionic surfactant to enhance the electrospinability and improve the morphology of electrospun nanofibers. Experiments have shown that polymer/surfactant can eliminate beads in nanofibers,25,26 and improve the mechanical properties of electrospun poly(vinyl alcohol) nonwoven mats.27 Use of a surfactant can enlarge the window of electrospinability.

EFFECT OF SURFACE TENSION ON THRESHOLD VOLTAGE

The mechanism of electrospinning is deceptively simple: in the absence of an electric field, a fluid forms a drop at the exit of a capillary, its size being determined by surface tension. When an electric field is present, it induces charges in the fluid. These quickly relax to the fluid surface, to name just a few. Recent studies on the nanostructure of goose down showed both the excellent thermal insulation and breathability of goose down.9,10

## INTRODUCTION

Electrospinning is a simple, versatile and powerful approach to producing nanofibers from various synthetic and natural polymers.1–5 Nanofibers sometimes behave extremely well in many respects due to nano-effects,6–8 for example remarkable strength, high surface energy and surface reactivity, and excellent thermal and electric conductivity, and serve as promising materials in nanotechnology and a highly versatile platform for a broad range of applications in widely different areas such as photonic structures, microfluidic channels (nanofluidics), catalysis, sensors, medicine, environmental engineering, defense and security, energy storage, invisibility devices (e.g. stealth aircraft and clothing) and radioprotection, to name just a few. Recent studies on the nanostructure of goose down showed both the excellent thermal insulation and breathability of goose down.9,10

The last decade of electrospinning technology has seen a sharp rise in fabrication and application of nanofibers.11–20 However, not every polymer can be prepared for electrospinning. Generally speaking solutions of polymers with too low or too high a molecular weight cannot be electrospun into continuous fibers. Electrospinnability mainly depends upon the solution viscosity,21 and vibration-electrospinning21–24 was designed to enhance electrospinnability markedly even for very high viscosity.22 In the work reported in this paper we used a non-ionic surfactant to enhance the electrospinability and improve the morphology of electrospun nanofibers. Experiments have shown that polymer/surfactant can eliminate beads in nanofibers,25,26 and improve the mechanical properties of electrospun poly(vinyl alcohol) nonwoven mats.27 Use of a surfactant can enlarge the window of electrospinability.

tension, the smaller the threshold voltage needed to overcome the surface tension of the electrospun solution. Surfactants can markedly reduce surface tension; as a result the electrospinnability can be enhanced. In the work reported in this paper, we added a non-ionic surfactant, Triton X-100, in a poly(vinyl pyrrolidone) (PVP) polymer solution to study the effects of surfactant on electrospinning.

EXPERIMENTAL

Materials
PVP (serial number K-30), Triton X-100 and absolute alcohol were purchased from Shanghai Chemical Reagent Co. Ltd, China. Deionized water was supplied by the College of Chemistry, Donghua University. A mixture of deionized water and absolute alcohol with a weight ratio 1:5 was used as solvent. All materials were used without further purification.

Instrumentation
The electrospinning setup consisted of a syringe, a needle, a grounded collector plate, a flowmeter and a variable DC high-voltage power generator (0–100 kV; f180-L, Shanghai Fudan high school). The scheme of the electrospinning process is shown in Fig. 1.

Electrospinning process
All concentration measurements were done by weight (w/w). A mixture of deionized water and absolute alcohol with a weight ratio 1:5 was used as solvent. PVP with a concentration of 35% was dissolved in the solvent. Triton X-100 was added into the solution obtained at ratios of 2, 5, 8, 11 or 14 wt%. The prepared solution was magnetically stirred at 40°C.

EFFECT OF SURFACE TENSION ON DIAMETER OF NANOFIBERS
The morphology of the electrospun PVP fibers was investigated using SEM (JSM-5610). The fiber mat was collected on a SEM disc and coated with gold before imaging. SEM micrographs are shown in Fig. 2.

Figure 1. Electrospinning setup.

Figure 2. SEM micrographs of electrospun fibers at different Triton X-100 concentrations (wt%): (a) 0, (b) 2, (c) 5, (d) 8, (e) 11, (f) 14; 1.5 kV cm⁻¹, 35 wt% PVP. The tip-to-collector distance was 10 cm. The applied voltage connected to the needle was 15 kV. All electrospinning processes were carried out at room temperature in a vertical spinning configuration.
Surface tension was markedly reduced when the surfactant, Triton X-100, was added to the solution (Fig. 3). Figure 4 shows that the average diameter of the fibers decreased as the concentration of Triton X-100 increased.

When a surfactant is added, the surface tension becomes smaller. Consider the initial stage of the ejection of the charged jet. According to Newton’s second law, we have

$$F_E - F_S = ma$$  \hspace{1cm} (1)

where $F_E$ is the electric force acting on the charged surface of the Taylor cone and $F_S$ is the surface tension of the Taylor cone. Addition of the surfactant results in smaller surface tension, $F_S$; as a result, a higher acceleration of the charged jet is estimated, and accordingly a higher velocity of the charged jet is anticipated. According to the conservation of mass during the electrospinning, we have

$$\pi r^2 \rho u = Q$$  \hspace{1cm} (2)

where $u$ is the velocity of the jet, $Q$ is the flow rate which remains unchanged during the electrospinning, $\rho$ is the density and $r$ is the radius of the nanofiber. We predict

$$r \propto u^{-1/2}$$  \hspace{1cm} (3)

This means that the addition of the surfactant results in smaller nanofibers. In our experiment, the average diameter of the fibers with 14% Triton X-100 is about 380 nm while the average diameter of the fibers without any surfactant is 1155 nm.

From Eqn (3), we obtain

$$\frac{dr}{dt} \propto u^{-3/2} \frac{du}{dt} \propto r^3 a$$  \hspace{1cm} (4)

or

$$\frac{dr^2}{dt} \propto a$$  \hspace{1cm} (5)

We can approximately write Eqn (5) in the form

$$r^2 \propto a t$$  \hspace{1cm} (6)

As the distance between the tip and the collector is fixed during the electrospinning, so the time for the jet to travel from the tip to the collector is assumed to be unchanged. We therefore have

$$r \propto a^{-1/2}$$  \hspace{1cm} (7)

In view of Newton’s second law, Eqn (1), we finally obtain the following relationship:

$$r = \frac{k}{\sqrt{F_E - F_S}}$$  \hspace{1cm} (8)

where $k$ is a constant. For our experiment, we obtain approximately (see Fig. 5)

$$r = \frac{711.6}{\sqrt{29.2 - F_S}}$$  \hspace{1cm} or  \hspace{1cm} $$d = \frac{1423.2}{\sqrt{29.2 - F_S}}$$  \hspace{1cm} (9)

where $d$ is the diameter in nm and $F_S$ is the surface tension in mN m$^{-1}$.

**EFFECT OF SURFACTANT ON ELECTROSPINABILITY**

Our experiment showed that when the concentration of PVP exceeded a critical value, 48%, it could not be successfully electrospun into a fiber. It looked like

![Figure 3. Surface tension of 35 wt% PVP solution with different Triton X-100 concentrations.](image_url)

![Figure 4. Average diameter of 35 wt% PVP nanofibers with different Triton X-100 concentrations.](image_url)

![Figure 5. Effect of the surface tension on the diameter of the electrospun nanofibers.](image_url)
an electrospay or a filament that broke up due to surface tension. However, the situation changed when Triton X-100 was added into the PVP solution. It was shown that even when the concentration of PVP reached 48%, the solution could be electrospun into nanofibers with a diameter of about 780 nm (Fig. 6).

CONCLUSIONS
Our experimental results show that the electrospinnability of a polymer solution depends on its concentration. Electrospun fiber diameter depends greatly on the surface tension. The surfactant Triton X-100 added in the solution dramatically decreased the fiber diameter, and also enhanced the electrospinnability.

We have also given a very simple theoretical prediction of the average diameter of the nanofibers under different surfactant concentrations. Our theoretical prediction agrees very well with our experimental observation.

ACKNOWLEDGEMENTS
This material is based on work supported by the National Natural Science Foundation of China under grant no. 10372021, the 111 project under grant no. B07024 and the Program for New Century Excellent Talents in University under grant no. NCET-05-0417. The experiment was conducted by the second author.

REFERENCES