POLYVINYL ALCOHOL/STARCH COMPOSITE NANOFIBERS BY BUBBLE ELECTROSPINNING

by

Zhi LIU [a,b] ***and Ji-Huan HE*** [*a,b]

[a] Nantong Textile Institute, Soochow University, Nantong, China
[b] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou, China

Original scientific paper
DOI: 10.2298/TSCI1405473L

Bubble electrospinning exhibits profound prospect of industrialization of macro/nano materials. Starch is the most abundant and inexpensive biopolymer. With the drawbacks of poor strength, water resistibility, thermal stability and processability of pure starch, some biodegradable synthetic polymers such as poly (lactic acid), polyvinyl alcohol were composited to electrospinning. To the best of our knowledge, composite nanofibers of polyvinyl alcohol/starch from bubble electrospinning have never been investigated. In the present study, nanofibers of polyvinyl alcohol/starch were prepared from bubble electrospinning. The processability and the morphology were affected by the weight ratio of polyvinyl alcohol and starchy. The rheological studies were in agreement with the spinnability of the electrospinning solutions.

Key words: *bubble electrospinning, polyvinyl alcohol, starch, composite*

Introduction

Macro/nano polymer fibers have attracted much attention in recent years because of their applications in areas such as high-performance filters, sensors, drug delivery, organic solar cells or food industry [1, 2]. Various methods have been developed to fabricate macro/nano polymer materials such as electrospinning, the template method and the bubble electrospinning [3, 4]. Compared with other methods, the bubble electrospinning showed the virtues of unlimited polymer solutions and good industrialization prospect, and has been shown to prepare various kinds of macro/nano polymer materials [5].

Among all natural biopolymers, starch has been considered as one of the most promising one because of its easy availability, biodegradability, and lower cost. Therefore, starch is widely used for biodegradable applications. However, pure starch lacks the strength, water resistibility, thermal stability and processability [6]. To improve some of these drawbacks, starch was often blended with some biodegradable synthetic polymers such as poly (lactic acid) (PLA), polyvinyl alcohol (PVA), which has good potentials for plastic and food packaging applications. PVA is a material with a high technological potential as a water-processable. However, PVA has low biodegradation rate and poor moisture barrier properties [7]. To improve its eco-friendliness and performance, PVA is usually modified with other polymers such as starch. Starch, PVA and starch/PVA have great potential for biodegradable plastic. Therefore, more attention must be paid to the composite of PVA and starch. However, the electrospinning of PVA and starch is little investigated, and the composite of PVA and starch from bubble electrospinning has never been studied.

* Corresponding author; e-mail: hejihuan@suda.edu.cn

In the present study, different weight ratio of starch and PVA were prepared for bubble electrospinning. The morphology of nanofibers was observed by SEM. Meanwhile, the rheological studies were carried out to analysis the processability of electrospinning solutions.

Experimental

Dissolving the soluble starch (AR, Shanghai, China) and PVA 1750 ± 50 (AR, Co., Ltd. China) in aqueous solution, regenerated solution concentration of 10 wt.% were obtained, and five weight ratio of starch and PVA were prepared for bubble electrospinning, which are called 10:0, 3:1, 1:1, 1:3, 0:10. A high electric potential of 20 kV was applied, and the electrospun nanofibers were collected on flat aluminum foil which was placed at a distance of 25 cm from the solution. The morphology of nanofibers was observed using an SEM (Hitachi S-4800, Japan) at 20 °C, 60 RH. Rheological studies were ran on a rheometer (Rheometer, TA Instruments) with a 35 mm cone plate (Ti, 35/1°). The normal force applied on the sample during lowering of the top plate was limited to 0.1 N. The shear rate was linearly increased from 0.1 to 5000 1/s at 25 °C.

Results and discussion

The morphology of the nanofibers was examined by SEM, as shown in fig. 1. It can be seen that when the pure starch or the weight ratio of starch/PVA is 3:1, there is no fibers formation, and only droplets were obtained. With the increase of PVA, the weight ratio is 1:1, 1:3 and pure PVA. It showed good processability, smooth morphology and uniform in diameter. Pure starch is difficult to process in traditional technology and room temperature, and the addition of PVA makes it good spinnability, as reported previously [8].

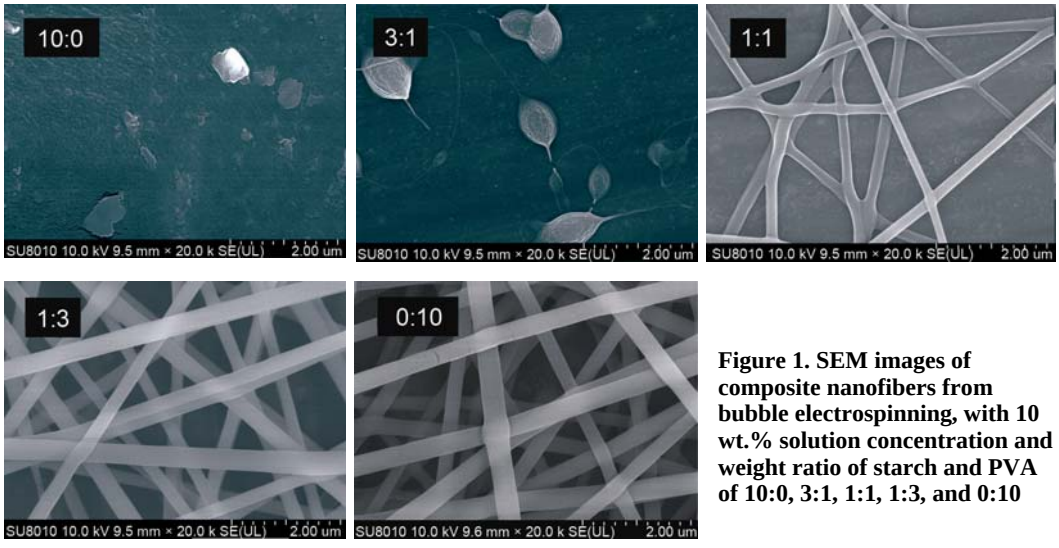

Figure 1. SEM images of composite nanofibers from bubble electrospinning, with 10 wt.% solution concentration and weight ratio of starch and PVA of 10:0, 3:1, 1:1, 1:3, and 0:10

The rheological behavior is closely related to the spinnability of polymer solution, and is also an indicator for macromolecule entanglements in solution. Figure 2 shows the flow curves of electrospinning solutions. It can be seen obviously that the difference of 10:0, 3:1 with 1:1, 1:3, and 0:10. When the ratio of starch/PVA is 10:0, 3:1, it showed strong shear thinning, and only droplets were obtained, as shown in fig. 1. The lower degree of entanglements of the macromolecules may lead to the shear thinning behavior, which might be a key factor prevent-

ing jet and fiber formation [9]. It is not shear thinning at low shear rates and only slightly at high shear rates when the ratio of starch/PVA is 1:1 and 1:3 (fig. 2). As a result, nanofibers formation were observed (fig. 1). With the increased ratio of PVA, the viscosities of the solution increased (fig. 2), making the increase in diameter of nanofibers, which are accordance with the previous reports.

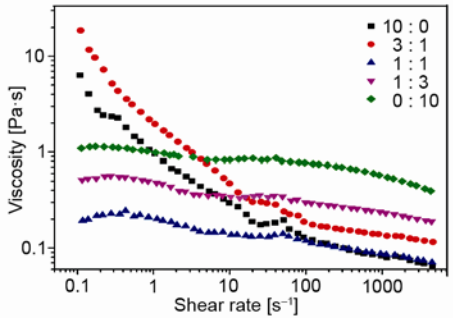

Figure 2. Rheological behaviors of 10 wt.% bubble electrospinning solutions, with weight ratio of starch and PVA of 10:0, 3:1, 1:1, 1:3, and 0:10

Conclusions

Composite nanofibers of starch and PVA were prepared from bubble electrospinning. Fiber formation was observed when the ratio of starch/PVA is 1:1 and 1:3, and it has good morphology of the nanofibers and good spinnability. The rheological studies were in accordance with the SEM results. It is not shear thinning at low shear rates and only slightly at high shear rates when the ratio of starch/PVA is 1:1 and 1:3, which makes it has good spinnability and good morphology of nanofibers. The composite nanofibers have great potential in plastic and food packaging applications.

Acknowledgments

The work is supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), National Natural Science Foundation of China under grant No.11372205 and Project for Six Kinds of Top Talents in Jiangsu Province under grant No. ZBZZ-035, Science & Technology Pillar Program of Jiangsu Province under grant No. BE2013072 and Natural Science Foundation of the Jiangsu Higher Education Institutions of China under grant No. 14KJA130001.

References

[1] Liu, Y., *et al*., High-Flux Microfiltration Filters Based on Electrospun Polyvinylacohol Nanofibrous Membranes, *Polymer, 54* (2013), 2, pp. 548-556
[2] Wenk, E., *et al*., Silk Fibroin as a Vehicle for Drug Delivery Applications, *Journal of Controlled Release, 150* (2011), 2, pp. 128-141
[3] Kong, L. Y., Ziegler, G. R., Fabrication of Pure Starch Fibers by Electrospinning, *Food Hydrocolloids, 36* (2014), May, pp. 20-25
[4] Huang, Y. C., *et al*., Transformation of Polymer Nanofibers to Nanospheres Driven by the Rayleigh Instability, *Applied Materials and Interfaces, 5* (2013), 8, pp. 3134-3142
[5] Dou, H., He, J.-H. Nanoparticles Fabricated by the Bubble Electrospinning, *Thermal Science, 16* (2012), 5, pp. 1562-1563
[6] Creek, J. A., *et al*., Amylose Crystallization from Concentrated Aqueous Solution, *Biomacromolecules, 7* (2006), 3, pp. 761-770
[7] Fathi, E., *et al*., Physically Crosslinked Polyvinyl Alcohol-Dextrin Blend Xerogels: Morphology and Thermal Behavior, *Carbohydrate Polymers, 84* (2011), 1, pp. 145-152
[8] Mizrahy, S., Peer, D., Polysaccharides as Building Blocks for Nanotherapeutics, *Chemical Society Reviews, 41* (2012), 7, pp. 2623-2640
[9] Kong, L. Y., Ziegler, G. R., Role of Molecular Entanglements in Starch Fiber Formation by Electrospinning, *Biomacromolecules, 13* (2012), 8, pp. 2247-2253

Paper submitted: January 3, 2014
Paper revised: April 2, 2014
Paper accepted: July 15, 2014