HIGHLY ALIGNED ELECTROSPUN NANOFIBERS BY HOT-DRAWING

by

Hong-Ying LIU [a,b]***, Lan XU*** [a,b*]***, and Qi-Long SUN*** [c]

[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
[c] School of Textile and Clothing, Nantong University, Nantong, China

Original scientific paper
DOI: 10.2298/TSCI1504357L

Aligned polyacrylonitrile nanofibers were prepared by a modified electrospinning. Hot-drawing was used to improve the properties of the obtained nanofibers. Experiment revealed great changes in degree of alignment, crystallization, exothermic peak, and mechanical properties of nanofibers.

Key words: *electrospinning, nanofiber alignment, hot-drawing, properties*

Introduction

Electrospinning is a simple method for generating ultrathin fibers with diameters ranging from tens of nanometers to tens of micrometers. With the development of science and technology, it is highly desirable to develop an approach that is able to generate well-aligned and better properties nanofibers. For example, in the fabrication of electronic and photonic devices, well-aligned and better properties are often required. The alignment of fibers can improve mechanical properties of fiber composites [1-4].

The mechanical strength of nanofibers can be increased by hot drawing. The drawing process orientates long molecules into alignment along the longitudinal axis of the nanofibers. The higher alignment of molecules increases the intermolecular bonds which causes higher mechanical strength. The orientation can also increase the crystallinity of nanofibers [5]. Leenslag and Penning, [6] and Postema and Penning [7] have increased the mechanical strength of their Poly(L-lactil acid) (P(L)LA) filaments remarkably by using hot-drawing temperatures near the melting temperature of polymer. Miaudet, *et al*. [8] use hot-drawing treatment to improve the properties of nanotube/polyvinyl alcohol (PVA) fibers. This treatment yields a crystallinity increase of the PVA and an unprecedented degree of alignment of the nanotubes.

In this paper, aligned polyacrylonitrile (PAN) nanofibers were prepared by a modified electrospinning with a positively charged ring between the needle and the parallel electrodes collector. We used hot-drawing treatments, a concept inspired from textile technologies, to improve the properties of the obtained nanofibers. The influence of hot-drawing treatments was researched on the degree of alignment, exothermic peak, crystallization, and mechanical properties of composite fibers. Results showed the crystalline microstructure of

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

the PAN nanofibers after hot-drawing treatment developed well, and the crystallinity, alignment degree, and tensile strength of the PAN nanofibers were improved.

Experiment

The PAN solutions were prepared with 10wt.% by using N, N-dimethylformamide. An electrospinning setup was modified by placing a positively charged ring between the needle and the parallel electrodes collector. Electrospinning experiments were carried out with the same collective distance (18 cm), voltage applied (15 kV), and flow rate (0.1 ml/h) at the room temperature (25 ºC), and 45% relative humidity in a vertical spinning configuration. The distance between the parallel electrodes collector is 4 cm. The applied ring voltage is +5 kV. The ring was 19 cm in diameter and the distance from the ring to the parallel electrodes collector was 5 cm. The obtained electrospun nanofibers were hot-drawing treated at 130 ºC.

Results and discussion

Figure 1 shows scanning electron microscopy pictures of the electrospun PAN nanofibers before and after hot-drawing treatment. The results the treatment enhanced the degree of the alignment of electrospun nanofibers. The thickened fibers are due to the mat shrinkage by the thermal treatment. This phenomenon is due to the fiber shrinkage occurred at elevated temperatures.

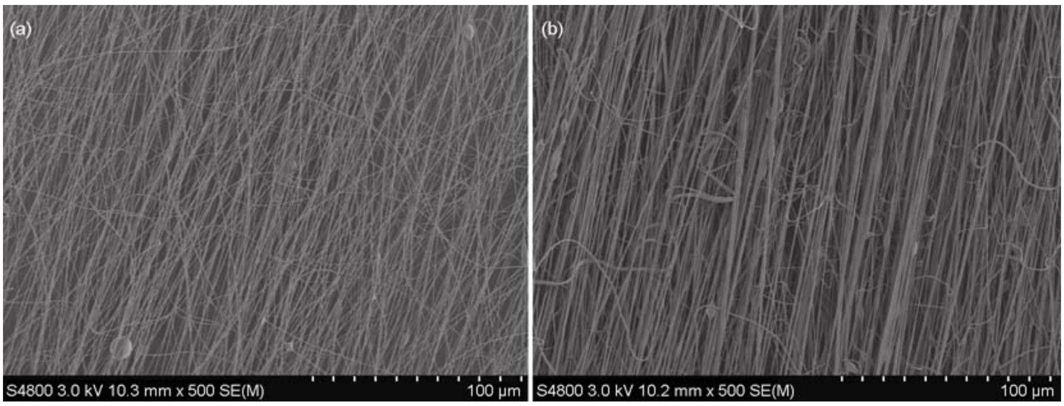

Figure 1. The SEM images of PAN nanofibers before and after hot-drawing treatment; (a) before hot-drawing treatment, (b) after hot-drawing treatment

The crystalline of the PAN was determined by an X-ray diffractometer (XRD). The XRD patterns of PAN before and after hot-drawing treatment were shown in fig. 2. It illustrated the crystal peaks of PAN obtained by hot-drawing treatment were sharpened which proved that the degree of crystallinity of the PAN was obviously increased by hot-drawing treatment.

Differential scanning calorimetry (DSC) thermograms of PAN nanofibers before and after hot-drawing treatment were shown in fig. 3. The nanofibers after hot-drawing treatment showed a relatively large and sharp exothermic curve with a peak at 300 °C. At the same time, the peak shifted toward the low temperature. This indicated that the crystalline microstructure of the nanofibers after hot-drawing treatment developed well. The results obtained from DSC were supported by XRD analysis.

Figure 4 shows the stress vs strain curves of PAN nanofibers before and after hot-drawing treatment. It was seen that treatment enhanced the tensile properties. That meant the tensile properties of PAN nanofibers were improved by hot-drawing treatment. The improvement in tensile properties was the result of the enhanced degree of alignment and crystallinity [9].

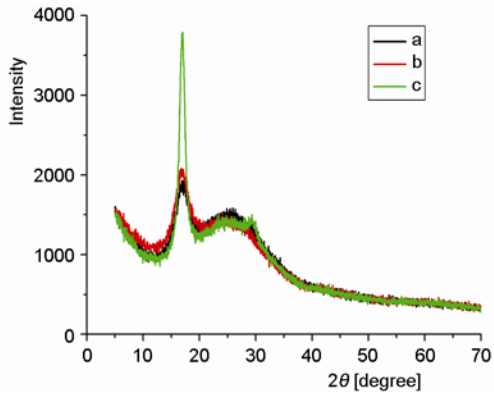

Figure 2. The XRD patterns of PAN nanofibers; (a) non-woven fabric, (b) before hot-drawing treatment, (c) after hot-drawing treatment

Conclusions

We used hot-drawing treatments, a concept inspired from textile technologies, to improve the properties of the aligned PAN nanofibers obtained by a modified electrospinning. Results showed the heat treatment could improve the degree of alignment of nanofibers. And the crystallinity of the hot-stretched fibrous membranes confirmed by X-ray diffraction analysis enhanced obviously. The exothermic peak temperature of the hot-stretched membranes confirmed by DSC decreased obviously. That meant the crystalline microstructure of the PAN nanofibers after hot-drawing treatment developed well, and the improved nanofiber alignment and crystallinity resulted in the increased tensile strength of the nanofibrous membranes. Hot-drawn PAN fibers hold great potential for a number of applications such as tissue engineering, electronic and photonic devices, and so forth.

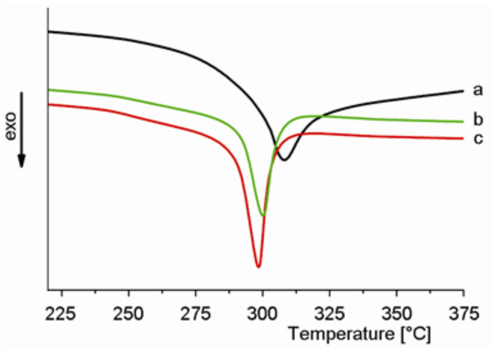

Figure 3. The DSC curves of PAN nanofibers; (a) non-woven fabric, (b) before hot-drawing treatment, (c) after hot-drawing treatment

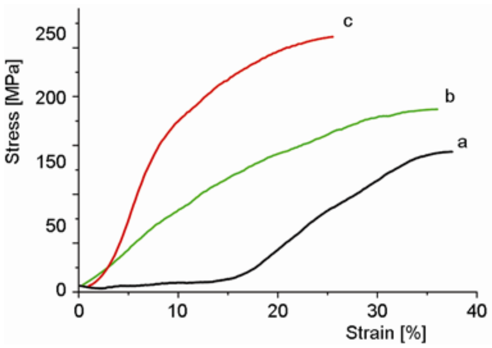

Figure 4. Stress *vs.* strain curves of PAN nanofibers; (a) non-woven fabric, (b) before hot-drawing treatment, (c) after hot-drawing treatment

Acknowledgments

The work is supported financially by PAPD (A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions), Jiangsu Provincial Natural Science Foundation of China (Grant No. BK20131175), Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 14KJA130001), Suzhou Science and Technology Project (Grant No. SYG201434), and Nantong Science and Technology Project (Grant No. BK2014050).

Reference

[1] Pagliara, S., *et al.*, Electrospun Light-Emitting Nanofibers as Excitation Source in Microfluidic Devices, *Lab on a Chip, 9* (2009), 19, pp. 2851-2856
[2] Meine, A. J., *et al.*, Optimization Strategies for Electrospun Silk Fibroin Tissue Engineering Scaffolds, *Biomaterials, 30* (2009), 17, pp. 3058-3067
[3] Zhu, Z., *et al.*, Aligned Electrospun ZnO Nanofibers for Simple and Sensitive Ultraviolet Nanosensors, *Chemical Communications, 18* (2009), May, pp. 2568-2570
[4] Tamura, T., *et al.*, Aligned Electrospun Nanofiber Composite Membranes for Fuel Cell Electrolytes, *Nano Letters, 10* (2010), 4, pp. 1324-1328
[5] Marja, R., *et al.*, Effect of Hot Drawing on Properties of Wet-Spun Poly(L,D-Lactide) Copolymer Multifilament Fibers, *Journal of Applied Polymer Science, 115* (2009), 1, pp. 608-615
[6] Leenslag, J. W., Pannings, A. J., High-Strength Poly(L-Lactide) Fibres by a Dry-Spinning/Hot-Drawing Process, *Polymer, 28* (1987), 10, pp. 1695-1702
[7] Postema, A. R., Pannings, A. J., Study on the Drawing Behavior of Poly(L-Lactide) to Obtain High-Strength Fibers, *Journal of Applied Polymer Science, 37* (1989), 8, pp. 2351-2369
[8] Miaudet, P., *et al.*, Hot-Drawing of Single and Multiwall Carbon Nanotube Fibers for High Toughness and Alignment, *Nano Letters, 5* (2005), 11, pp. 2212-2215
[9] Liu, H., *et al.*, Thermal Treatment for Nanofibrous Membrane, *Thermal Science*, *18* (2014), 5, pp. 1673-1675

Paper submitted: January 10, 2015
Paper revised: May 5, 2015
Paper accepted: May 12, 2015