EFFECTS OF STRETCHING ON STRUCTURES AND PROPERTIES OF CONTINUOUS AND UNIAXIALLY ALIGNED ELECTROSPUNG POLYACRYLONITRILE NANOFIBER BUNDLES

Jie Liu [1,], Gui Chen [1], Hao Fong [2]*

1. College of Materials Science and Engineering, Beijing University of Chemical Technology, Chao-Yang District, Beijing 100029, China
2. Department of Chemistry, South Dakota School of Mines and 8 Technology, 501 East St. Joseph Street, Rapid City, South Dakota 57701, USA

Introduction

That the large length to diameter ratio of carbon nanofibers is larger than traditional carbon fibers endues it with remarkable qualities. However, mechanical properties of as-electrospun PAN nanofibers is poor because of limited crystallinity and orientation which is caused by huge elongation rate during electrospinning process, particularly during bending instability. In general, the higher degree molecular orientation exist in the original PAN precursor fiber, the better mechanical properties particularly the tensile modulus carbon fibers own [1]. So, the same as traditional fibers, the as-electrospun PAN nanofibers also need to be stretched subsequently which can result in higher molecular orientation, higher crystallinity, and finally mechanical property improvements of carbon nanofibers.

In this paper, instead of using roller, new flow water bath combining with existing wet spinning process and static water bath collection method [2] was adopted as the collector. Using a representative PAN copolymer as the initial sample, we successfully prepared continuous and uniaxially aligned as-electrospun nanofiber bundles，which were subsequently stretched in boiling water under tension. Structures and properties of the nanofiber bundles before and after stretching were investigated.

Experimental

The bottom image in Fig. 1 schematically shows our electrospinning experimental setup, which consisted of the specially designed bullet-shaped spinneret, a high voltage power supply purchased from the Gamma High Voltage Research, a laboratory-made water bath device and the roller with a diameter of ~17 cm. During electrospinning, a positive high voltage of 25kV was applied through a metal rod to a solution (16 wt% PAN copolymer in DMF; the commercial PAN copolymer precursor fibers were provided by the Courtaulds, Ltd.) held inside the spinneret, which was placed 13 cm above flow water bath collector, and the rotational speed of the roller was set at 130 rpm. Overall, due to the dual action of the water and the roller, the as-electrospun nanofibers bundles do have a high degree of alignment along the axial direction and the surface of nanofibers appeare to be very smooth, as seen in Fig. 2(a). Subsequently, PAN as-electrospun nanofiber bundles were stretched in boiling water (about 97°C) to different times of their original lengths with the bundles under tension.

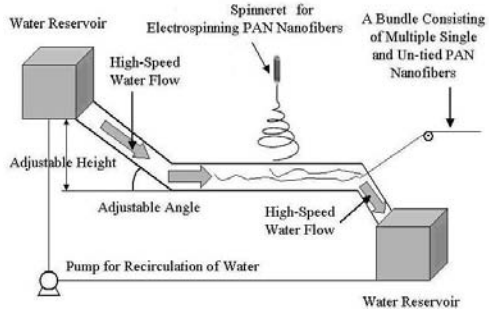
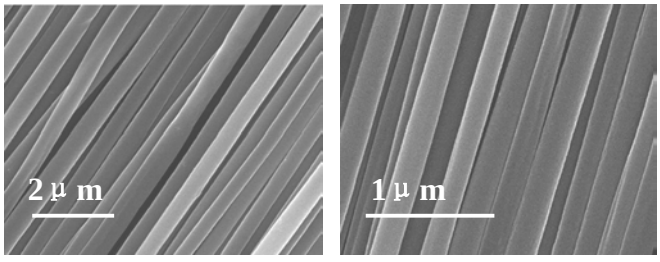


Fig. 1 Schematic representation of the electrospinning setup for preparing continuous and uniaxially aligned nanofibers

Results and Discussion

The SEM images, as shown in Fig. 2, present that, as compared to the as-electrospun nanofiber bundles, the stretched nanofiber bundles possessed higher degrees of alignment. In addition, referring to Fig. 3 (a), we note that diameter of nanofiber bundles decreases with the increase of stretching ratio, whereas density increases.

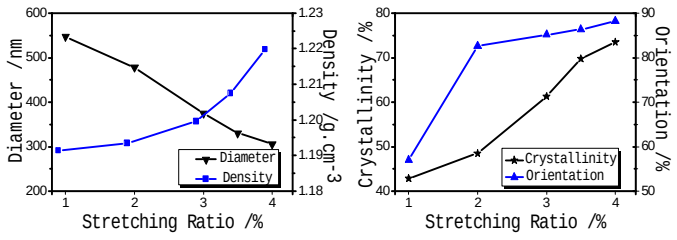


(a) (b)

Fig. 2 SEM images showing the representative morphologies of the electrospun PAN nanofiber bundles (a) before and (b) after stretching

The crystalline and macromolecular structures and orientations in nanofiber bundles before and after stretching were investigated by XRD. The XRD profiles was recorded

with the 2 θ angles from 5 to 40° at the scanning speed of 5 ℃/min. Results of the XRD experiments are shown in Fig. 3(b). The crystallinity and macromolecular orientation increase with the increase of stretching ratio. As shown in Fig. 4 (a)， all fibers show a strong diffraction peak centered at the 2θ angle of 16.7° and a weak diffraction peak center at the 2θ angle of 29.5° . The intensity of these two peaks apparently increases with the increase of stretching ratio.



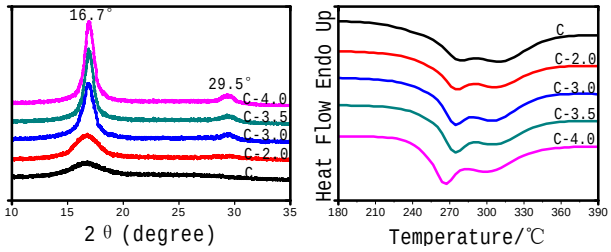
(a) (b)

Fig. 3 Effect of stretching on (a) diameter and density, (b) crystalinity and orientation of PAN nanofiber bundles

This is because PAN can be divided into crystalline part and amorphous part and its crystal form is hexagonal para-crystal state. When nanofibers are stretched in boiling water under tension, PAN molecular chains in amorphous part and crystal grain will be predominant orientated along the tension direction. There will be some orderly texture of PAN macromolecular chains in amorphous part when stretching before it crystallizes. Then |ΔS | will decrease, |ΔH |> T |ΔS | and the formula ΔF=ΔH - TΔS < 0 holds. Finally, crystallization of PAN will go smoothly.

PAN macromolecular chains arrange closely along the axial direction of fibers under tension and pile into compact structures orderly, and lots of DMF solvent contained in the fiber rapidly removes during the stretching process, which jointly result in the increase of fibers' density.

The studies on thermo-chemical behaviors of as-electrospun and stretched bundles were investigated by DSC operating at conditions of air atmospheres , the flow rate of 20 mL/min, heated and scanned from 40 to 400℃ with the rate of 5℃/min. Results of the DSC experiment are shown in Fig. 4(b). It indicate that, with the increase of stretching ratio, the exothermic onset temperature and the peak temperature is lower while the heat evolved is higher. This is because PAN intramolecular cyclization occurs only in isotactic conformation district during thermal stabilization of PAN fibers. When the fibers are stretched in boiling water under tension, the molecular chains possess predominant orientation along the external forces direction and conformation-specific reverse of some macromolecular chains occurs simultaneously in amorphous region. This causes the increase of chain regularity, and the cyclization reaction processes easier. It is showed as the exothermic onset temperature and the peak temperature are lower than stretched before. At the same time, stretching causes proportion increase of the isotactic conformation district and the order region. Thus, the number of molecules that could process cyclization reaction increases, and then heat evolved of cyclization reaction increases which is showed as the gradually increased intensity of the first exothermic peak with the increase of stretching ratio in Fig. 4(b).



(a) (b)

Fig. 4 (a) XRD and (b) DSC curves of as-electrospun PAN nanofiber bundles (C) and nanofibers with different stretching ratios, such as 2.0,3.0,3.5,4.0

Conclusion

In this study, continuous and uniaxially aligned PAN as-electrospun nanofiber bundles were prepared by a nanomaterials processing technique of electrospinning. Stretching can improve alignment of nanofibers, make nanofibers densified, have large ratio of length to diameter, increase crystallinity and ordering, and remove residual solvent. So it is meaningful for increasing the tensile strength of nanofibers.

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References

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