PREPARATION OF PAN-BASED CARBON NANOFIBERS BY HOT-STRETCHING

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Abstract

Partially aligned and oriented polyacrylonitrile (PAN) nanofibers were electrospun from PAN solution including dimethylformamide for the preparation of carbon nanofibers. The as-spun polyacrylonitrile nanofibers was hot-stretched by weighing metal in a temperature controlled oven to improve its crystallinity and molecular orientation. Then it were stabilized at 250 □ under the stress, and carbonized at 1000 ℃ in N_2 by fixing the length of the stabilized nanofiber to convert them into carbon nanofibers. The average diameter of carbon nanofibers were 140 nm. The crystallinity of the stretched fibers confirmed by *X*-ray diffraction analysis has enhanced 4 -fold in comparison with that of as-spun fibers. The improved fiber alignment and crystallinity resulted in the increased modulus and tensile strength of the nanofibers as much as 5.7- and 4.7-fold, respectively. The tensile strength and the modulus of carbon nanofiber increased up to 2243±120 MPa and 170±15.8 GPa, respectively. Thus, the hot-stretched nanofiber can be used as a promisable precursor to produce high-performance carbon composites.

1. Introduction

Electrospinning from polymer solutions can produce fibers having diameters in the nanometer to micron range, with the sizes depending on the electrostatic force applied [1]. Carbon nanofibers have recently received increased attention due to their potential uses such as composite reinforcing fillers, heat-management materials, high-temperature catalysts, membrane-based separation media, and components in nanoelectronics and photonics [2]. However, the mechanical properties of electrospun nanofibers need to be improved because of limited crystallinity and orientation during the whirlpool jet spinning without stretching [3].

Polyacrylonitrile (PAN) is a common precursor of general carbon fibers. During the stabilization, PAN was stretched to improve the molecular orientation, which resulted in the enhanced crystallinity and mechanical properties of the fibers [4-7]**.** Also, the electrospun PAN nanofiber needs a stretching to improve the crystallinity and molecular orientation. Unfortunately, there was no attempt on nanofiber stretching as yet owing to such small diameter of fiber and the poor alignment of the as-spun nanofiber sheet. Therefore, hot-stretching of the electrospun PAN nanofiber as the form of sheet was tried in this study.

The purpose of this work is a stretching-induced alignment of electrospun PAN nanofibers in the sheet to improve the fiber alignment and crystallinity. To achieve the purpose; (i) PAN nanofiber sheet was prepared by electrospinning of PAN solution, (ii) hot-stretching of sheet was carried out by weighing metal in a temperature controlled oven, and (iii) characterization of the sheet was carried out to confirm the improved fiber alignment and crystallinity, and the increased mechanical properties.

2. Experimental

2.1 Preparation of electrospun PAN nanofiber sheet

The required PAN solution was prepared from a commercial PAN fiber (UK Courtaulds Ltd.) composed of PAN/methyl acrylate/itaconic acid (93:5.3:1.7 w/w, average molecular weight of 100,000 g/mol). The solvent employed was *N,N*-dimethylformamide (DMF, Beijing Chemical Plant Co.). The PAN solution was prepared by dissolving 11 wt % chopped 2-3mm length PAN fibers into the DMF solvent, and homogenized by ultrasonic mixing.

The electrospinning apparatus consisted of a dual syringe infusion pump, a high voltage power supply, and a rotating drum for gathering the nanofibers. The PAN solution was placed in a vertically-aligned glass syringe with 0.5 mm diameter pinhead opening. An electrode was fixed to the pinhead and connected to a power supply that could generate a DC voltage up to 25 kV. The rotating drum was placed under the syringe infusion pump, and served as both a ground counter electrode and the nanofiber collector. The distance and voltage between pinhead and nanofiber collector were set to 17 cm and 10 kV, respectively.

A paper frame having a rectangular opening (4 cm x 16 cm) was fixed to the rotating drum as shown in Figure 1(a) and (b). Two hours of electrospinning were performed to obtain a 17 μm thickness nanofiber sheet. This 17 μm was the optimum thickness to prepare a uniformly electrospun sheet under the applied arbitrary conditions. Figure 1(c) shows the as-spun PAN nanofiber sheet.

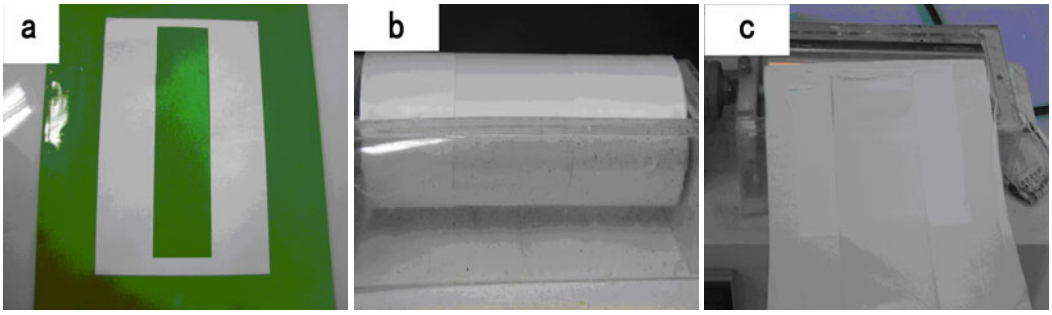

Figure 1. Preparation of the nanofiber sheets: (a) paper frame, (b) rotating drum, and (c) as-spun nanofiber sheet.

2.2 Hot-stretching

The nanofiber sheet (4 cm width x 10 cm length x 17 μm thickness) was hot stretched as following the suggestion by Phillip and Johnson[8,9], which is the key process during the manufacturing of carbon fibers. Both ends of the sheet were clamped with pieces of graphite plates. Then, one end was fixed to the ceiling of the oven and the other end was weighted by 75 g of metal poise to give a desired tension and elongation in the temperature-controlled oven at 135 ±2 °C for 5 minutes. The stretching ratio, λ , was calculated from $\lambda = L/L_0$, where L and L_0 are the lengths of nanofiber sheet after and before the hot-stretching, respectively.

2.3 Characterization

The unidirectional alignment and the diameter change of the nanofiber in the sheet was observed by scanning electron microscope (SEM, HITACHI S-4700 FEG-SEM). The cross sectional view of a nanofiber and the thickness of sheet were obtained by (i) embedding a sheet in resin, (ii) immersing it in liquid nitrogen, and (iii) fracturing it perpendicular to the fiber alignment direction to expose the cross-section area.

The crystallinities of the as-spun and the hot-stretched PAN nanofiber were investigated with *X*-ray diffractometer (XRD, Rigaku D/max 2500VB2+ /PC), operated at 40 kV and 200 mA to produce Cu Kα radiation (λ = 1.54 Å). The percent crystallinity (PC) was obtained by extrapolation of the crystalline and amorphous parts of the diffraction pattern [13]. The Hermans orientation coefficient, f , was determined using the primary equatorial arcs from the *(100)* reflection at $d \approx 5.3$ Å as the following equation [10,11]:

$$f = \frac{\int_0^{90} \frac{(3\cos^2\beta - 1)}{2} I \sin\beta d\beta}{\int_0^{90} I \sin\beta d\beta} \qquad (1)$$

Where, β is the azimuthal angle between the axis of the molecular segment and the fiber alignment, and I is the scattering intensity of the *(100)* reflection at that angle. The crystallite size was calculated using the formula $L_c = k\lambda / (\beta\cos\theta)$, with k = 0.89 and λ = 1.54 Å [10].

Modulus and tensile strength of 5 mm x 20 mm size sheet were measured before and after stretching using an Instron 1185 (Electromechanical Universal Testing Machine). The average cross sectional area of nanofibers was calculated from the weights of the specimens and the density of PAN (1.2 g/cm^3).

3. Results and Discussion

Relatively aligned PAN nanofibers were obtained by electrospinning with the rotating drum at high-spun speed. However, the whirlpool jet from the pinhead to the collector made it difficult to get unidirectional alignment in a large-area sheet. Therefore, the electrospun nanofiber sheet needs a subsequent hot-stretching to improve the fiber alignment in the sheet.

Figure 2(a) shows SEM observation of the as-spun PAN nanofibers in a sheet. The enlarged photo shows the rough surface of nanofiber. Usually nanofibers did not align well when the surface of the nanofibers was rough. Figure 2(b) shows the hot-stretched nanofibers, proving the excellent alignment along the sheet axis. However, the fiber surface was still rough, possibly as a result of imposed tension. When 75 g of metal poise was used to provide the tension, the size of the sheet specimen changed from 4 cm width x 10 cm length to 2 cm width x 17 cm length, resulting in the stretch ratio of 1.7. If the tension increased, the stretching ratio and the alignment may increased, but too much increase may resulted in the rupture of the sheet.

Figures 2(c) and (d) show cross-sectional views of as-spun and hot-stretched nanofibers in the sheet. The remarkable changes were the decrease in fiber diameter and the increase of the crystallinity, which are usually the keys to fabricate the nanofibers with high mechanical properties[6].

Figure 3 shows *X*-ray diffraction (XRD) patterns from the as-spun and the oriented nanofibers in a sheet. The XRD patters were collected from the bundle of sheets. There were two diffraction peaks at 17 and 29° which were corresponding to

the $d \approx 5.3$ Å from the (*100*) and the $d \approx 3.03$Å from the (*110*) reflections respectively [12]. The diffraction pattern of the as-spun nanofiber showed one weak peak with a value of 2 θ at 17°. This indicates that electrospinning of the nanofibers onto a rotating drum generates limited crystallinity. In contrast, the oriented nanofibers show two diffraction peaks indexed with values of 2 θ of 17 and 29°. The former, very strong peak corresponds to the (*100*) diffraction planes of the crystallite, and the latter to the (*110*) planes [12]. The degree of orientation is usually expressed by orientation coefficient, which can be calculated from the half-width of the corresponding peak in the XRD curve.

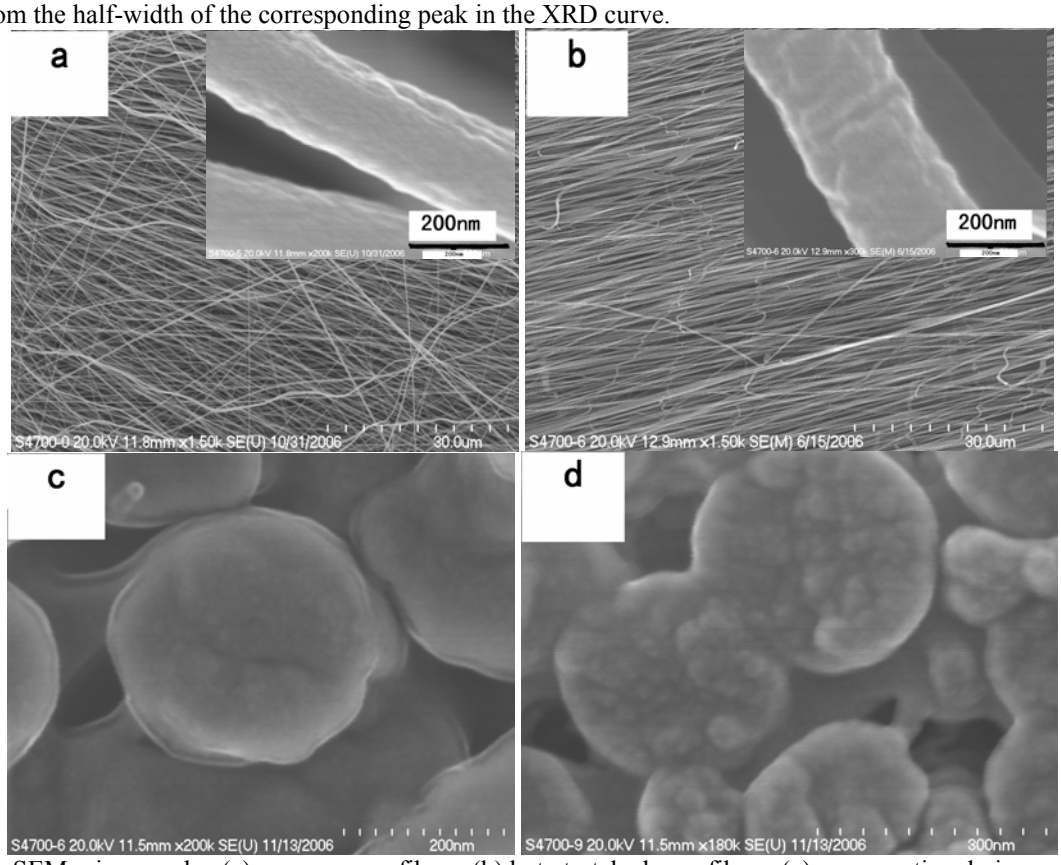

Figure 2. SEM micrographs: (a) as-spun nanofibers, (b) hot-stretched nanofibers, (c) cross sectional views of as-spun nanofibers and (d) hot-stretched nanofibers.

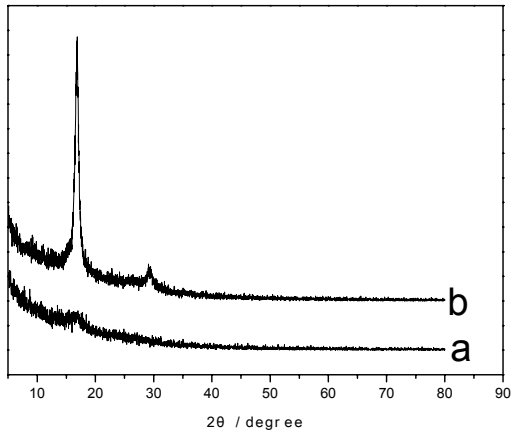

Figure3. *X*-ray diffraction patterns for the nanofibers: (a) as-spun, and (b) highly oriented.

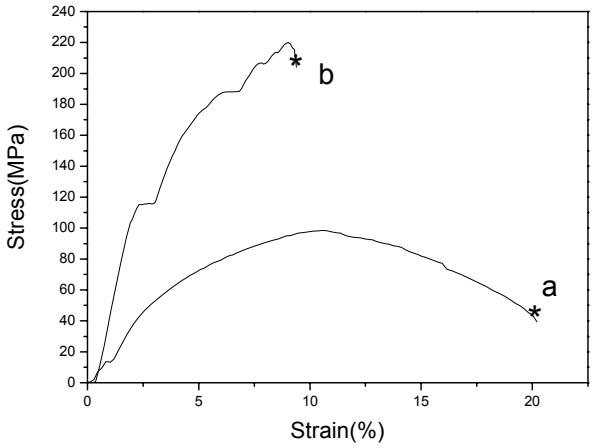

Figure 4. Stress–strain curves for the nanofiber sheets: (a) as-spun, and (b) highly oriented. The star symbols locate the rupture points of the samples.

Table 1 presents values of the percent crystallinity (PC) and the orientation coefficient for the two types of nanofibers. The percent crystallinity of the hot-stretched nanofiber increased as much as four-fold and the orientation coefficient increased 22% in comparison with those of as-spun nanofiber. The crystallite size also decreased about 10%.

Table 1 Percent crystallinity and orientation coefficient of nanofibers obtained from *X*-ray diffraction curves

Nanofiber	Percent crystallinity (%)	Orientation coefficient (%)	Crystallite size (Å)
As-spun	7.92	45.6	2.51
Hot-stretched	31.8	55.4	2.26

Figure 4 shows the stress–strain curves of the nanofiber sheet before and after hot-stretching at 135°C for 5 min. The stress of the as-spun fiber sheet increased gradually to a maximum value of approximately 100 MPa at around 10% strain, and then decreased with further increase in the strain. In contrast, the hot-stretched sheet showed stresses that increased rapidly to the maximum value of around 220 MPa.

The mechanical properties of the sheets are summarized in Table 2. The hot-stretched nanofiber sheet was higher in tensile strength but lower in extensibility, relative to the sheet containing the as-spun nanofibers. Specifically, the modulus of the sheet increased by a factor of approximately 5.7, the strain at break decreased by approximately 50 %, and the tensile strength at break point increased by a factor of around 4.7. Five nanofiber sheets were tested in each sample to get the average Young's modulus, breaking elongation, elongation strength, and stress-strain curves at room temperature.

Table 2 Mechanical properties of the nanofiber sheets

Nanofiber	Modulus (MPa)	Strain at break point (%)	Stress at break point (MPa)
As-spun	425 ± 30	20	45±4
Hot-stretched	2440 ±115	9.5	210±10

The observed decrease in extensibility upon improvement in other mechanical properties is often the cost or trade-off experienced in optimizing the mechanical properties of a material. In the present case, increasing orientation and degree of crystallinity obviously affected different properties in very different ways. The results presented here, however, certainly encourage further work establishing the sets of conditions that would give the best balance of properties for a given application.

4. Conclusions

Polyacrylonitrile nanofiber sheet was prepared by electrospinning from PAN/N,N-dimethylformamide solution, and hot-stretched to increase the degree of crystallinity and molecular orientation of the nanofiber. Improved unidirectional alignment and decrease of the fiber diameter were observed by scanning electron microscopy in the stretched sheet. The crystallinity of the stretched sheet confirmed by *X*-ray diffraction analysis has enhanced 4-fold in comparison with that of as-spun sheet. The improved fiber alignment and crystallinity resulted in the increased modulus and tensile strength of the nanofiber sheet as much as 5.7- and 4.7-fold, respectively. Thus, the hot-stretched nanofiber sheet can be used as a promisable precursor to produce high-performance carbon nanofiber composites. The mechanical properties of the PAN nanofiber sheet can be improved more by extensive studies of electrospinning and hot-stretching conditions.

Acknowledgements

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References

1. Hammel, E. Tang, X. Trampert M, Schmitt T, Mauthner K, Eder A, Pötschke P. 2004. Carbon nanofibers for composite applications. *Carbon* 42: 1153–1158.
2. Chand, S. Carbon Fibers for Composites. 2000. Carbon fibers for composites. *Journal of Materials Science* 35:1303–1313.
3. Li, D. Wang, Y. Xia, Y. 2003. Electrospinning of Polymeric and Ceramic Nanofibers as Uniaxially Aligned Arrays. *Nano Letters* 3:1167-1171.
4. McCann, J.T. Marquez, M. Xia, Y. 2006. Highly Porous Fibers by Electrospinning into a Cryogenic Liquid. *Journal of American Chemical Society* 128:1436-1437.
5. Zussman, E. Chen, X. Ding, W. Calabri, L. Dikin, D.A. Quintana, J.P. Ruoff, R.S. 2005. Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers. *Carbon* 43: 2175–2185
6. Dror, Y. Salalha, W. Khalfin, R.L. Cohen, Y. Yarin, A.L. Zussman, E. 2003. Carbon Nanotubes Embedded in Oriented Polymer Nanofibers by Electrospinning. *Langmuir* 19:7012-7020
7. Watt, W. Perov, B.V. eds. 1985 "Handbook of Composites Vol 1, Strong Fibers" Amsterdam
8. Johnson, J. Phillips, L.N. Watt, W. Brit Patent 1,110,790, 1965.
9. Johnson, J. Watt, W. Phillips, L.N. Moreton, R. Brit Patent 1,166,251, 1966.
10. Norman, W.H. Cheetham, W.H. Tao, L. 1998. Variation in crystalline type with amylose content in maize starch granules: an X-ray powder diffraction study. *Carbohydrate Polymers* 36:277-284.
11. Lafrance, C.P. Pezolet, M. Prud'homme, R.E. 1991. Study of the distribution of molecular orientation in highly oriented polyethylene by x-ray diffraction. *Macromolecules* 24:4948-4956.
12. Fennessey, S.F. Farris, R.J. 2004. Fabrication of aligned and molecularly oriented electrospun polyacrylonitrile nanofibers and the mechanical behavior of their twisted yarns. *Polymer* 45:4217–4225.