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Effects of carbonization tension on the structural and tensile properties of continuous bundles of highly aligned electrospun carbon nanofibers

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ABSTRACT

The ultimate goal of this study was to further improve tensile properties of continuous bundles of highly aligned carbon nanofibers. The hypothesis was that adopting moderate tension during carbonization could improve the formation and orientation of graphite crystallites, leading to increased tensile properties of carbon nanofibers. In this study, bundles consisting of highly aligned PAN copolymer nanofibers were first prepared by electrospinning and collected *via* a flowing water bath, followed by 3-time stretching and oxidative stabilization. The stabilized PAN nanofibers were then carbonized under tensions of 10–50 cN which corresponding to 254.7–1273.5 MPa, respectively. The effects of carbonization tension on structural and tensile properties of carbon nanofibers were investigated by WAXD, Raman spectroscopy and filament specimen methods. The results indicated that the orientation of graphite crystallites in carbon nanofibers could be improved by increasing carbonization tensions from 254.7 MPa to 509.4 MPa; and the highest tensile strength and modulus of carbon nanofibers could reach 1115 MPa and 194.5 GPa, respectively.

1. Introduction

Electrospun polyacrylonitrile (PAN)-based carbon nanofibers (CNFs), with fiber diameter in the range of hundreds of nanometers, have great potential to achieve dramatically enhanced mechanical properties compared with traditional micron-sized counterparts [1–9]. This is because the ultrasmall fiber diameters of CNFs result in reduced structural imperfection and sheath/core structure, which are the most crucial barriers to significantly improve the mechanical strength and modulus of the carbon fibers (CFs) [1–7,10–13]. Meanwhile, the surface area of CNFs increases dramatically along with reduced fiber diameter, and this can facilitate the solid-gas two phase carbonization reaction [5]. Consequently, the evolution of structure features of PAN nanofibers during the carbonization process is different compared with micron-sized fibers, and many effort have been devoted to improve the structure and mechanical properties of CNFs through controlling carbonization [1,2,7,10–13].

Zhou et al. increased the tensile strength and Young's modulus of CNFs from 325 to 542 MPa and 40 to 58 GPa, respectively, by increasing carbonization temperatures from 1000 to 2200 °C [7]. Arshad et al. prepared CNFs with final carbonization temperatures from 1400 to 1700 °C, and increased their tensile strength and Young's modulus to 3.5 GPa and 172 GPa, respectively [1]. Liu et al. also found that the tensile strength and Young's modulus of CNFs could be increased from 299 to 306 MPa and 49 to 69 GPa with increasing carbonization temperatures from 400 to 1000 °C [10]. It is well established that the tensile properties of CNFs could be greatly enhanced through increasing carbonization temperatures. However, the study on carbonization tension, which is another key factor affecting the mechanical properties of CNFs, is quite limited.

Tension during carbonization is an important factor affecting the mechanical properties of CFs, because it can alter the orientation of graphite microstructures in carbon fibers; and highly aligned graphite crystallites along the fiber axis is a characteristic factor of high strength CFs [14,15].

In this study, effects of carbonization tension on the structural and tensile properties of CNFs were investigated. Continuous bundles of highly aligned PAN nanofibers were prepared *via* electrospinning, followed by washing, drying densification, stretching, and oxidative stabilization [4,6,8,9]. The stabilized PAN nanofibers were carbonized under N_2 atmosphere with various applied carbonization tensions. The mechanical properties of resulting CNFs were characterized by filament specimen methods. WAXD and Raman spectroscopy were used to characterize the formation and orientation of graphite crystalline of carbon nanofibers.

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2. Materials and methods

The PAN copolymer used in this study was the Special Acrylic Fibers (SAF3K) provided by Courtaulds in the U.K. Electrospinning process was adopted with a laboratory-produced system with recirculated flowing water bath for the collection of as-electrospun nanofibers. The details of electrospinning process could be obtained in our previous publication [6]. The bundles of as-electrospun PAN nanofibers were then stretched to ~3 times of their original lengths in an environment of saturated steam of ~0.4 MPa [6]. Stabilization of PAN nanofiber precursors were carried out with 3 gradient temperature zones of 260/275/285 °C with 5 min duration in each zone (Fig. 1A). The stabilized nanofibers were subsequently treated with low temperature carbonization at 350–700 °C for ~4 min and high temperature carbonization at 700–1350 °C for ~6 min in a tube furnace filled with high purity nitrogen gas (Fig. 1B). The tension applied on the nanofiber bundles during carbonization was adjusted to 10, 20, 30, 40, 50 cN (denoted as CNF-10, CNF-20, CNF-30, CNF-40, CNF-50), corresponding to 254.7, 509.4, 764.1, 1018.8, and 1273.5 MPa, respectively.

The graphite structures in carbon nanofibers were investigated by WAXD with equatorial and meridional scanning. The equatorial scanning could determine the average interplanar spacing "$d_{(002)}$" according to "Bragg Equation", the crystallite sizes of "L_c" (the thickness of graphite sheets) and "$L_{a\perp}$" (the width of graphite sheets) according to "Scherrer Equation" [7,12,15]. The meridional scanning could determine the crystallite size of "$L_{a\parallel}$" (the length of graphite sheets) according to "Scherrer Equation", either [7,12,15]. The azimuthal scanning of WAXD was carried out to investigated the degree of orientation of graphite structures "f_c" determined by the "Herman's Equation" [3,4,6]. Raman spectroscopy was introduced to characterize the amount of structurally ordered graphite crystallites through "*R*-value" determined by "*D*-band" and "*G*-band" in Raman spectra of carbonaceous materials [7,10,12,15]. Tensile properties including tensile strength and modulus of carbon nanofibers were measured by filament testing method.

3. Results and discussion

Fig. 2A showed the SEM images of continuous bundles of highly aligned electrospun PAN carbon nanofibers (CNFs) collected using water bath. It could be observed that the CNFs prepared in this study had average diameters of 119 ± 9 nm and possessed unidirectional alignment and narrow diameter distribution (Fig. 2B). The smooth fiber morphology enabled the uniform distribution of applied tension on fibers during carbonization, which could ensure the accurate investigation of the effect of tension on the mechanical properties of CNFs.

To explore the mechanical properties of CNFs prepared under different carbonization tension, their tensile strength and Young's modulus were measured. A typical stress-strain curve of CNF-20 was given in Fig. 3A. It was shown that the fibers deformed linearly until failure. The tensile strength and Young's modulus, as a function of carbonization tension, of each sample was summarized in Fig. 3B. The tensile strength and Young's modulus of CNFs first increased with carbonization tension from 10 to 20 cN, then decreased as the applied tension further increased to 50 cN. This demonstrated that the carbonization tension had great influence on the mechanical properties of CNFs. The highest tensile strength of 1115 ± 163 MPa and the highest modulus of 194.5 ± 69 GPa were both achieved under carbonization tension of 20 cN. It was reported that the high strength and high modulus of CFs originated from the high alignment and strong bonding of graphite-like flake structure of carbon [14,15]. In this study, there supposed to be no significant difference between the graphite microcrystal size of each sample, since their carbonization temperatures, which determine the degree of graphitization, were identical [1,7,12,14,15]. Thus, the increased strength and modulus of CNFs were likely attributed to the improved alignment of graphite crystalline as a result of increased tension.

Fig. 3C showed the equatorial and meridional WAXD scanning curves of CNFs. Based on these curves, the structural parameters of $d_{(002)}$, L_c, and L_a (including $L_{a\perp}$and $L_{a\parallel}$) were characterized and listed in Table 1 [7,15]. All samples showed similar $d_{(002)}$ (3.56–3.59 Å), L_c (1.59–1.66 nm), $L_{a\perp}$ (2.38–2.52 nm) and $L_{a\parallel}$ (3.62–3.91 nm); and these structural parameters were not correlated with the increasing of carbonization tension. The virtually identical crystalline structures of CNFs prepared with different carbonization tension was in agreement with our previous assumption that the carbonization temperature determined the graphite crystalline structures, and the carbonization tension had no significant influence on the formation of graphite crystallites.

Azimuthal scanning (2θ=25.5°) was employed to characterized the orientation of graphite crystallites (f_c) in CNFs prepared under

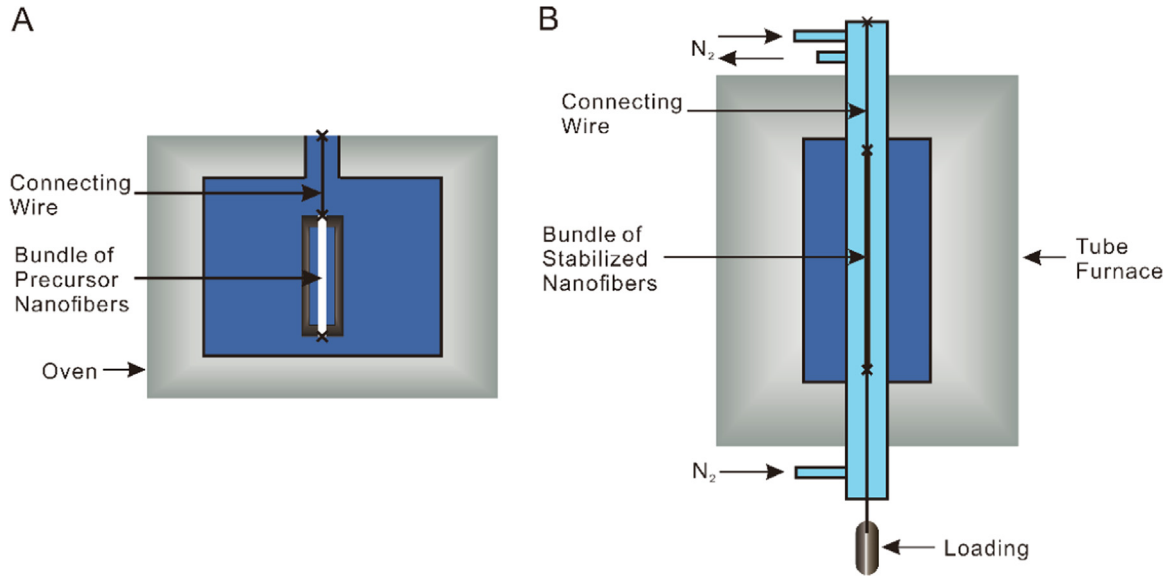

Fig. 1. Schematic diagrams showing the setup for (A) oxidative stabilization and (B) carbonization of the electrospun PAN nanofiber bundles with different tension.

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