High Strength Electrospun Single Copolyacrylonitrile (coPAN) Nanofibers with Improved Molecular Orientation by Drawing

Tang-Cheng Xu\textsuperscript{a}, Dong-Hua Han\textsuperscript{b}, Yong-Mei Zhu\textsuperscript{a}, Gai-Gai Duan\textsuperscript{b}, Kun-Ming Liu\textsuperscript{c}, and Hao-Qing Hou\textsuperscript{a,*}

\textsuperscript{a} Department of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China
\textsuperscript{b} Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China
\textsuperscript{c} School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Abstract High-performance carbon nanofibers are highly dependent on the performance of their precursors, especially polyacrylonitrile (PAN). In this work, the copolymer of PAN (coPAN) was synthesized for electrospinning. A self-assembling set-up was used for the stretching of single coPAN nanofibers. FTIR and Raman spectroscopies were used to characterize the chemical structure of coPAN nanofibers. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to monitor the morphology of single coPAN nanofibers under different drawing times. Micro-tensile test was used to determine the mechanical properties of single coPAN nanofibers. The results indicated that the drawing led to an increase in degree of molecular orientation along the fiber axis from 0.656 to 0.808, tensile strength from 304 MPa to 595 MPa, and modulus from 3.1 GPa to 12.4 GPa. This research would provide fundamental information of high-performance electrospun coPAN nanofibers and offer opportunities for the preparation of high-performance carbon nanofibers.

Keywords Single nanofiber; Electrospinning; Polyacrylonitrile; Molecular orientation; Mechanical property

INTRODUCTION

Carbon fibers are well-known for their excellent mechanical properties, especially high strength and high modulus.\cite{11-13} They have found many applications in sports and leisure products, spaceships, artificial satellites, space shuttles, missiles, and so on.\cite{6,7} Since 1960s, carbon fibers have started to be developed in China, while 90% of the high-performance carbon fibers are from abroad.\cite{8} The main reason is that the quality of carbon fiber, especially their mechanical properties cannot satisfy the practical applications. At present, many kinds of materials, such as polyimide,\cite{9,12} pitch,\cite{13,14} cellulose,\cite{15,16} polyacrylonitrile (PAN)\cite{17,18} are reported as the precursor for the preparation of carbon fibers. Among these precursors, PAN have attracted the most attention because of its high carbon yield and good mechanical and thermal performance. In actual, during the preparation of carbon fibers, the quality of PAN significantly limits the development of carbon fibers. To solve the issues of low strength and defects of precursor, and further improve the structure and properties of carbon fibers, the primary and important issue is to investigate the structures and properties of the PAN precursor fibers.

* Corresponding authors, E-mail: duangaigai@njfu.edu.cn (G.G.D.)

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Many strategies have been reported to improve the mechanical performance of PAN fibers, such as drawing,\cite{20,21} copolymerization,\cite{9,22} blending,\cite{23} and adding organic and inorganic fillers.\cite{24,25} One of the important approaches is to prepare PAN nanofibers with diameter as small as possible.\cite{26} Electrospinning is an efficient way to produce high-performance nanofibers with diameter in the range from sub-nanometers to micrometers.\cite{27-35} Dzenis et al. reported that as the diameter of PAN electrospun nanofibers decreased, single PAN electrospun nanofiber could simultaneously possess high strength and toughness.\cite{26} They ascribed such phenomenon to the high degree of chain alignment coupled with low crystallinity. Zhou et al. found that the addition of phosphoric acid was efficient to increase the mechanical properties of PAN-based electrospun carbon nanofibers.\cite{24} Duan et al. applied copolymerization with oxygen-containing monomer and added oxygen-containing blending component, poly(amic acid), respectively, which could significantly decrease the pre-oxidation temperature and finally improve the mechanical properties of PAN-based electrospun carbon nanofibers.\cite{22} Duan et al. also reported the effect of molecular weight on the mechanical properties of PAN nanofibers.\cite{36} They found as the molecular weight increased, PAN nanofibers exhibited increased mechanical properties. Recently, Greiner’s group fabricated PAN nanofiber yarns for hot-draw- ing, which led to significant improvement in tensile strength and modulus.\cite{37}
All the above reports ascribe the reasons for the excellent mechanical performance to the better molecular orientation. However, the direct relationship between the degree of molecular orientation and the mechanical properties is absent. In addition, because of the difficulties of handling single nanofiber, there are still few reports regarding the drawing of single PAN electrospun nanofiber and the effect of drawing ratio on the degree of molecular orientation and their mechanical performance.

In this work, we synthesized the copolymer of PAN (coPAN) by copolymerization from acrylonitrile (AN), n-butyl acrylate (BA) and itaconic acid (ITA) for electrospinning. The addition of oxygen-containing comonomers of BA and ITA is facial for the cyclization in the pre-oxidation process toward the high-performance carbon nanofibers. A facial and easy setup was designed for collecting and drawing of single PAN electrospun nanofiber, and the effect of drawing ratio on the microstructures, degree of molecular orientation, and mechanical properties has been investigated. This study will provide potential outstanding PAN electrospun nanofibers for the preparation of high mechanical performance carbon nanofibers.

**EXPERIMENTAL**

**Materials**

Acrylonitrile (AN, AR, HANERCHEM Ltd., Guangzhou, China), n-butyl acrylate (BA, ≥98%, Alfa Aesar Ltd., Tianjin, China) and itaconic acid (ITA, ≥99%, J&K Scientific Ltd., China) were purified by distillation. Azobisisobutyronitrile (AIBN, AR, HANERCHEM Ltd., Guangzhou, China) was purified by recrystallization before use. Dimethyl sulfoxide (DMSO, AR, Jiangsu Qiangsheng Chemical Co., China) and N,N′-dimethylformamide (DMF, AR, Shanghua Runjie Chemical Co., Ltd.) were used as received.

**Preparation of coPAN Solution**

The co-PAN solution (30 wt%) was prepared from reaction of monomers AN, BA and ITA with 97/2/1 weight ratio in DMSO at 45−55 °C for 24 h in N2 atmosphere (Fig. 1a). The reaction was initiated by AIBN (0.2 wt% to the monomers). The intrinsic viscosity of the coPAN solution was 4.2 dL/g.

**Electrospinning of coPAN**

The above coPAN solution was diluted to 7.5 wt% by DMF for electrospinning. The electrospinning was performed under an electric field of 60 kV/m with a collecting distance of 20 cm. During electrospinning, the environment temperature and humidity were 23 °C and 30%, respectively. The fibrous mat was obtained using a steel mash as collector with a collecting time of 15 min. The single nanofibers for drawing were collected by a self-assembly set-up as shown in Fig. 1b. Two metal plates were fixed on the syringe pump. Before fixing, the metal plates were pasted by double-sided tapes to fix the single nanofiber. During electrospinning, the single nanofibers were fallen down. At this stage, the electrospinning time was around 5 s until 5−8 single fibers were collected by the plates.

**Drawing of Electrospun coPAN Nanofibers**

Before drawing, the unparallel single nanofibers were removed by the tweezers. The rest of single nanofibers were drawn by the syringe pump (Fig. 1c). The initial distance (L0) between the two plates was 2.00 cm. Then the fibers were drawn with a speed of 0.012 mm/s by the syringe pump to a pre-fixed length (L). The drawing times (λ) could be obtained from the ratio of L/L0. Due to the residual solvent in the single fibers, the single fiber can be stretched up to 2.2 times of the L0. The drawn fiber with drawing times (λ) of 1.0, 1.4, 1.8 and 2.2 were obtained finally while further higher drawing times could not be achieved in this work.

Fig. 1 Schematic process for the preparation, drawing and micro-tensile testing of single coPAN electrospun nanofibers: electrospinning (a, b), drawing (c), single fiber preparation (d), fiber diameter determination (e), and single fiber tensile testing (f).
Single Fiber Tensile Test

The stretched nanofibers were shifted into a paper frame (gauge length of 5 mm) one by one with double-sided tape to fix the fiber (Fig. 1d). Before the tensile testing, the single nanofiber on the paper frame was observed by atomic force microscopy (AFM III, Shanghai Zhoulun, China) to obtain its diameter (Fig. 1e). The single nanofiber on the paper frame was fixed on a micro-tensile tester (USF10, Powereach, Shanghai) with a micro-load sensor (ULA-2GR, Minebea Co., Ltd.) (Fig. 1f). During tensile test, a tensile speed of 0.094 mm/min was applied. At least five samples of single coPAN electrospun nanofiber were prepared for tensile test.

Characterization

Scanning electron microscopy (Tescan vega 3) and atomic force microscopy (AFM III, Shanghai Zhoulun, China) were used to observe the morphology of nanofibers. Before SEM measurement, all the samples were coated with gold for 120 s to enhance the electron conductivity of samples. FTIR (Bruker Tensor 27) and Raman spectroscopies (LabRAM HR-800, Horiba Jobin Yvon) were used to characterize the chemical structures. Polarized Raman spectroscopy with high resolution (XY<1 μm; Z<2 μm) and He-Ne laser light (632.8 nm) was used to determine the molecular orientation of coPAN in the nanofibers. During the measurement, the single nanofiber was perpendicular to the plane of light scattering.

RESULTS AND DISCUSSION

FTIR and Raman Spectroscopies

Generally, the chemical compounds do not have a symmetric center, and many groups often have both infrared activity and Raman activity. For materials with both activities, the positions of the spectral bands corresponding to the same vibration modes are theoretically the same. However, there are still some minor differences between these two approaches because of the different resolution. Therefore, the FTIR and Raman bands may not agree well. Possible deviations would be observed from the FTIR and Raman spectroscopies for the same group. As shown in Fig. 2 and Table 1, the strong band at 2240 cm$^{-1}$ in FTIR spectrum is the typical band for PAN molecules, which can be ascribed to the stretching vibration of C≡N [38]. The same group exhibits an absorption at 2246 cm$^{-1}$ in Raman spectrum [38,41]. The bands at 2935 and 2869 cm$^{-1}$ in FTIR spectrum are from the stretching vibration of −CH$_2$− and −CH− [42] while three bands at 2950, 2920 and 2895 cm$^{-1}$ were observed in Raman spectrum for the same groups [38,41]. The medium band at 1730 cm$^{-1}$ in FTIR spectrum could be attributed to the vibration of C=O from the comonomer of BA [38] while the same band was difficult to be observed in Raman spectrum. More band assignments could be found in Table 1. All these band assignments proved that the coPAN was successfully synthesized.

Effect of Drawing on Diameter of coPAN Nanofibers

SEM was used to evaluate the quality of electrospun coPAN nanofibers. As shown in Figs. 3(a) and 3(b), the coPAN nanofibers are uniform and smooth with average diameter of 715±42 nm. These defect-free coPAN nanofibers are the basic guarantee for the high mechanical performance. Figs. 3(c)−3(f) are the AFM images for the single coPAN nanofibers with different drawing times. All the nanofibers in AFM images are uniform and smooth, which is in accordance with the SEM results. The nanofiber without drawing (λ=1.0) presented similar diameter (718.5 nm) to the average diameter from SEM observation, proving the good quality of electrospun coPAN nanofibers. As increasing the drawing times to 1.4, 1.8 and 2.2, the diameter decreased to 614.3, 549.2 and 506.2 nm, respectively. Such significant decrease in diameter suggests that the coPAN molecules are not straight in the pristine nanofibers, which makes the stretching of the coPAN nanofiber possible. In addition, the diameter after drawing could be theoretically calculated from the following equations, when assuming the volumes of the nanofiber before ($V_0$) and after ($V$) the drawing are the same.

\[
V = V_0
\]

\[
V = \frac{1}{4}\pi d^2L = \frac{1}{4}\pi d_0^2L_0 = V_0
\]

\[
\lambda = \frac{L}{L_0}
\]

where $d_0=718.5$, and $\lambda=1.0$, 1.4, 1.8 and 2.2. Therefore, the theoretical diameters after drawing could be obtained as shown in Table 2. The result indicated that the theoretical diameters agreed well with the experimental data from AFM with a deviation below 4.30%.

Effect of Drawing on Molecular Orientation of coPAN Molecules in Nanofibers

Polarized FTIR and polarized Raman spectroscopies are two effective approaches for determining the degree of molecular orientation in the electrospun nanofibers [42−45]. However, polari-

Table 1 Band assignment of coPAN nanofibers by FTIR and Raman spectroscopies.

| Wavenumber (cm$^{-1}$) | Assignment |
|-----------------------|------------|
| FTIR                  | Raman      |
| 2935                  | 2950, 2920 | CH$_2$, CH |
| 2869                  | 2895       | CH          |
| 2240                  | 2246       | C=N         |
| 1730                  |            | C=O         |
| 1624                  |            | C=N, C=C    |
| 1452                  | 1458       | CH$_2$      |
| 1357                  | 1376−1274  | CH, NH      |
| 1253                  | 1318       | CH$_2$      |
| 1072                  | 1111       | C=N, C=O    |

*See https://doi.org/10.1007/s10118-021-2516-0 for the full text*
zed FTIR is usually performed on the nanofiber membranes or nanofiber bundles, but difficult for the measurement of single nanofiber. In comparison, polarized Raman spectroscopy can overcome the above problem and is facial for the determination of molecular orientation in nanofiber. Fig. 4(a) shows the polarized Raman spectra in perpendicular \( XX \) and \( YY \) directions. Here, the characteristic band for the \( \text{C}≡\text{N} \) group was selected for the calculation of orientation degree (\( P \)):

\[
P = 1 - \frac{I_{XX}}{I_{YY}}
\]

where \( I_{XX} \) and \( I_{YY} \) are the intensities of the bands at \( XX \) and \( YY \) directions, respectively. The \( \lambda \) dependent \( P \) is plotted in Fig. 4(b). As the \( \lambda \) increased, the \( P \) also increased. When the single nanofiber is not mechanically stretched (\( \lambda = 1.0 \)), the \( P \) is 0.656, which could be due the electric-force induced molecular stretching during the formation of nanofibers. As \( \lambda \) increased to 1.4, 1.8, and 2.2, the \( P \) also increased to 0.703, 0.767, and 0.808, which are 7.2%, 16.9%, and 23.2% higher than the value of the un-

| Drawing times | Diameter (nm) | Deviation (%) |
|---------------|---------------|---------------|
| \( \lambda = 1.0 \) | 718.5 | – |
| \( \lambda = 1.4 \) | 614.3 | 606.8 | 1.22 |
| \( \lambda = 1.8 \) | 549.2 | 535.5 | 2.49 |
| \( \lambda = 2.2 \) | 506.2 | 484.4 | 4.30 |

Fig. 3  SEM image of electrospun coPAN nanofibers (a), corresponding fiber diameter distribution (b), and AFM images (c–f) of single coPAN nanofiber with different drawing times (\( \lambda \)=1.0, 1.4, 1.8 and 2.2).

Table 2  Summary of experimental and theoretical diameters after drawing with \( \lambda \)=1.0, 1.4, 1.8 and 2.2.

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The coPAN single nanofiber without stretching showed a tensile strength, modulus and strain at break of 304 MPa, 3.1 GPa and 189%, respectively. As the drawing times increased to 1.4, 1.8, and 2.2, both the strength and modulus increased to 367/420/595 MPa and 6.6/10.2/12.4 GPa, which are 21%/38%/95% and 113%/229%/300% higher than those of nanofibers with $\lambda=1.0$. However, the strain at break of the coPAN single nanofibers with $\lambda=1.4$, 1.8, and 2.2 decreased to 96%, 60%, and 24%, respectively. The trend of strength, modulus, and strain at break could be because of the drawing-induced molecular orientation along the nanofiber axis, as proved by the polarized Raman spectroscopy (Fig. 4).

![Polarized Raman spectroscopy of single electrospun coPAN nanofibers (a) and corresponding drawing-induced molecular orientation degree (b).](image)

The excessive drawing may damage the molecular structure of the fiber and cause various defects. Therefore, novel design on the drawing set-up under heating could be efficient to further increase the drawing times and finally increase the molecular orientation and mechanical performance.

**Effect of Drawing on Mechanical Properties of coPAN Single Electrospun Nanofiber**

Drawing is an efficient approach for improving the molecular orientation along the fiber axis and enhancing the mechanical properties. In this work, the drawing times dependent mechanical properties are shown in Fig. 5 and summarized in Table 3.

![Stress-strain curves of single coPAN electrospun nanofibers with different drawing times.](image)

| Drawing times | Tensile strength (MPa) | Tensile modulus (GPa) | Strain at break (%) |
|---------------|------------------------|-----------------------|---------------------|
| 1.0           | 304±25                 | 3.1±0.2               | 189±20              |
| 1.4           | 367±32                 | 6.6±0.5               | 96±12               |
| 1.8           | 420±37                 | 10.2±0.9              | 60±4                |
| 2.2           | 595±55                 | 12.4±1.0              | 24±1                |

To show the excellent mechanical properties of single coPAN electrospun nanofibers in this work, an Ashby figure of strength versus modulus was plotted for different PAN based electrospun nanofibers and other electrospun single nanofibers. As shown in Fig. 6(a), the single coPAN electrospun nanofibers occupy a very important area, which achieve high strength and high modulus, simultaneously. The mechanical properties of the single coPAN nanofibers after drawing in this work are higher than those of other electrospun PAN-based fibers, such as electrospun PAN yarns,[46,47] single PAN nanofibers,[48] electrospun PAN bundles under drawing,[49] aligned coPAN nanofibers,[50] and comparable to the yarns under stretching times of 2−6[37] and carbon nanotube (CNT) reinforced PAN nanofibers.[31,39−43] In addition, the mechanical performance of single coPAN nanofiber is also superior to that of most other electrospun polymeric single fibers, such as Nylon,[54] PAN,[56] polycaprolactone (PCL),[55] thermoplastic polyurethane (TPU),[56] polystyrene (PS),[56] PS/TPU/PS triaxial,[56] and TPU/PS core/shell,[56] except the high performance single polyimide (PI) electrospun nanofiber[57] (Fig. 6b).
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**Fig. 6** Ashby plots of strength versus modulus of electrospun PAN-based materials (a) and other electrospun single fiber (b). Yarn, [46, 47] PAN-CNT [21, 30–52] single nanofiber, [48] bundle (drawing), [49] coPAN (aligned) [56] yarn (A=2–6), [57] PI, [58] Nylon, [59] PAN, [59] PCL, [59] TPU, [59] PS, [59] PS/TPU/PS triaxial, [59] TPU/PS core/shell, [59] and coPAN (this work).
The image contains a page of a scientific document with references to various research papers. The text is dense and technical, discussing topics such as polymer materials, nanofibers, and their properties. The references are cited to support the claims made in the document. The page appears to be from a scientific journal, given the style and format of the references and the dense scientific language used.

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