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

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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

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INTRODUCTION

Carbon fibers are well-known for their excellent mechanical properties, especially high strength and high modulus.[1−5] They have found many applications in sports and leisure products, spaceships, artificial satellites, space shuttles, missiles, and so on.[6,7] Since 1960s, carbon fibers have started to be developed in China, while 90% of the high-performance carbon fibers are from abroad.[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,[9−12] pitch,[13,14] cellulose,[15,16] polyacrylonitrile (PAN),[17−19] 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.

Many strategies have been reported to improve the mechanical performance of PAN fibers, such as drawing,[20,21] copolymerization,[9,22] blending,[23] and adding organic and inorganic fillers.[24,25] One of the important approaches is to prepare PAN nanofibers with diameter as small as possible.[26] Electrospinning is an efficient way to produce high-performance nanofibers with diameter in the range from sub-nanometers to micrometers.[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.[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.[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.[23] Duan *et al*. also reported the effect of molecular weight on the mechanical properties of PAN nanofibers.[36] They found as the molecular weight increased, PAN nanofibers exhibited increased mechanical properties. Recently, Greiner's group fabricated PAN nanofiber yarns for hot-drawing, which led to significant improvement in tensile strength and modulus.[37]

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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.[38,39] 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 N_2 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-assembling set-up as shown in Fig. 1(b). 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 (L_0) 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/L_0. Due to the residual solvent in the single fibers, the single fiber can be stretched up to 2.2 times of the L_0. 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.

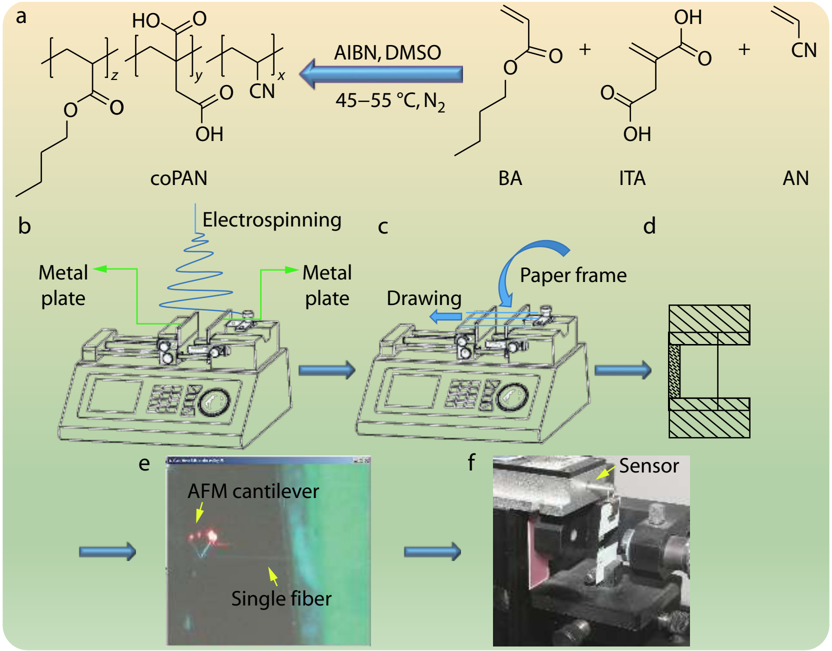

Fig. 1 Schematic process for the preparation, drawing and micro-tensile testing of single coPAN electrospun nanofibers: electrospinning (a, b), drawing (c), single fiber preparation (d), fiber diameter determination (e), and single fiber tensile testing (f).

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 Zhuolun, China) to obtain its diameter (Fig. 1e). The single nanofiber on the paper frame was fixed on a micro-tensile tester (JSF10, 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 Zhuolun, 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 $C\equiv N$.[39] The same group exhibits an absorption at 2246 cm^{-1} in Raman spectrum.[40,41] The bands at 2935 and 2869 cm^{-1} in FTIR spectrum are from the stretching vibration of $-CH_2-$ and $-CH-$,[38] while three bands at 2950, 2920 and 2895 cm^{-1} were observed in Raman spectrum for the same groups.[40,41] 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.

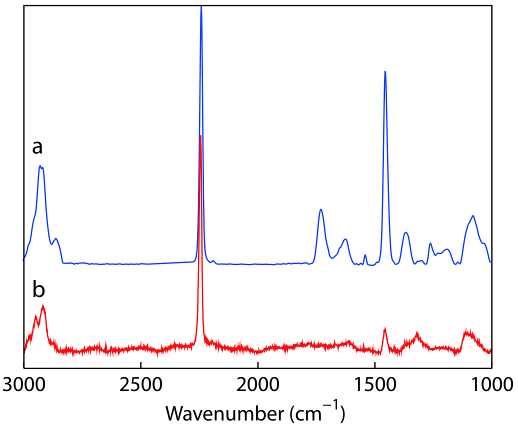

Fig. 2 FTIR (a) and Raman (b) spectra of coPAN nanofibers.

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	$C\equiv N$
1730	–	$C=O$
1624	–	$C=N$, $C=C$
1452	1458	CH_2
1357	1376–1274	CH, NH
1253	1318	CH_2
1072	1111	$C-N$, $C-O$

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 ($\lambda=1.0$) 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.

$$V = V_0 \tag{1}$$

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

$$\lambda = \frac{L}{L_0} \tag{3}$$

where d_0=718.5, and λ=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 spectroscopes are two effective approaches for determining the degree of molecular orientation in the electrospun nanofibers.[42–45] However, polari-

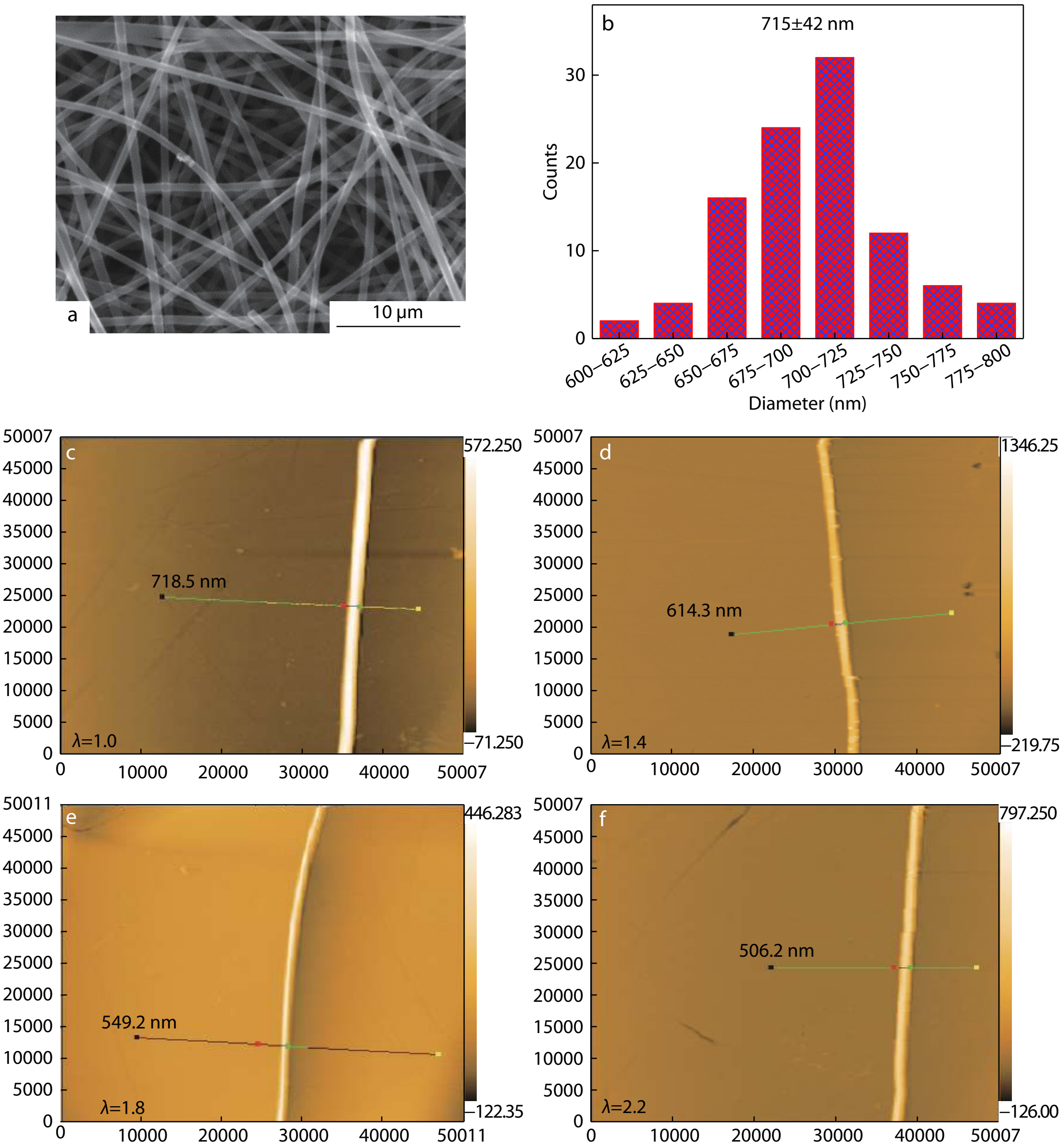

Fig. 3 SEM image of electrospun coPAN nanofibers (a), corresponding fiber diameter distribution (b), and AFM images (c–f) of single coPAN nanofiber with different drawing times (λ=1.0, 1.4, 1.8 and 2.2).

Table 2 Summary of experimental and theoretical diameters after drawing with λ=1.0, 1.4, 1.8 and 2.2.

Drawing times	Diameter		Deviation (%)
	AFM	Theoretical	
λ=1.0	718.5	–	–
λ=1.4	614.3	606.8	1.22
λ=1.8	549.2	535.5	2.49
λ=2.2	506.2	484.4	4.30

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 C≡N group was selected for the calculation of orientation degree (*P*):[37]

$$P = 1 - \frac{I_{XX}}{I_{YY}} \quad (4)$$

where I_{XX} and I_{YY} are the intensities of the bands at *XX* and *YY* directions, respectively. The λ dependent *P* is plotted in Fig. 4(b). As the λ increased, the *P* also increased. When the single nanofiber is not mechanically stretched (λ=1.0), the *P* is 0.656, which could be due the electric-force induced molecular stretching during the formation of nanofibers. As λ 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-

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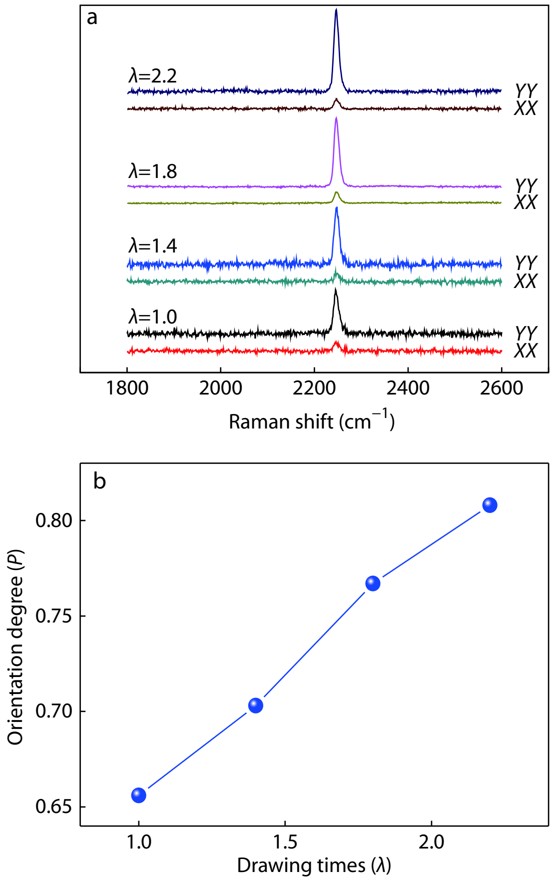

Fig. 4 Polarized Raman spectroscopy of single electrospun coPAN nanofibers (a) and corresponding drawing-induced molecular orientation degree (b).

drawing single nanofiber. In addition, during the experiment, it can also be found that as the draft ratio λ increased, fiber breakage would occur during the drawing process.

The main reason may be that the macromolecular chains in the nanofiber are in curl state at low drawing times and the residual solvent has a plasticizing effect on drawing. Therefore, it is relatively easy for the mechanical stretching. As the λ gradually increases, the fiber diameter decreases and the molecular chain is extended along the fiber axis, so the drawing becomes more and more difficult. When applying the λ to 2.2, more and more nanofibers are broken during the stretching. This phenomenon indicated that although the drawing can greatly improve the mechanical properties of single coPAN nanofibers, the drawing times is limited at room temperature. 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.

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 λ=1.0. However, the strain at break of the coPAN single nanofibers with λ=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).

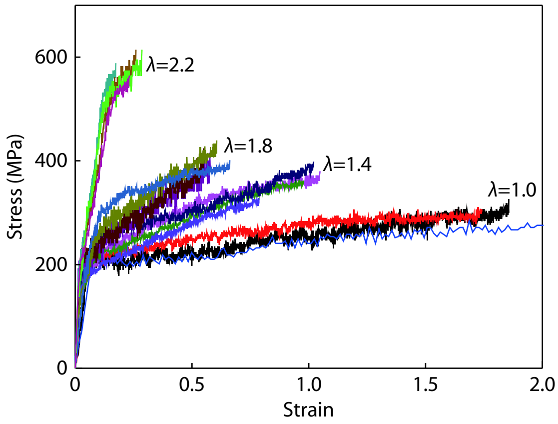

Fig. 5 Stress-strain curves of single coPAN electrospun nanofibers with different drawing times.

Table 3 Summary of mechanical properties of coPAN single electrospun nanofiber.

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,[36] and comparable to the yarns under stretching times of 2–6[37] and carbon nanotube (CNT) reinforced PAN nanofibers.[21,50–52] In addition, the mechanical performance of single coPAN nanofiber is also superior to that of most other electrospun polymeric single fibers, such as Nylon,[53,54] PAN,[26] 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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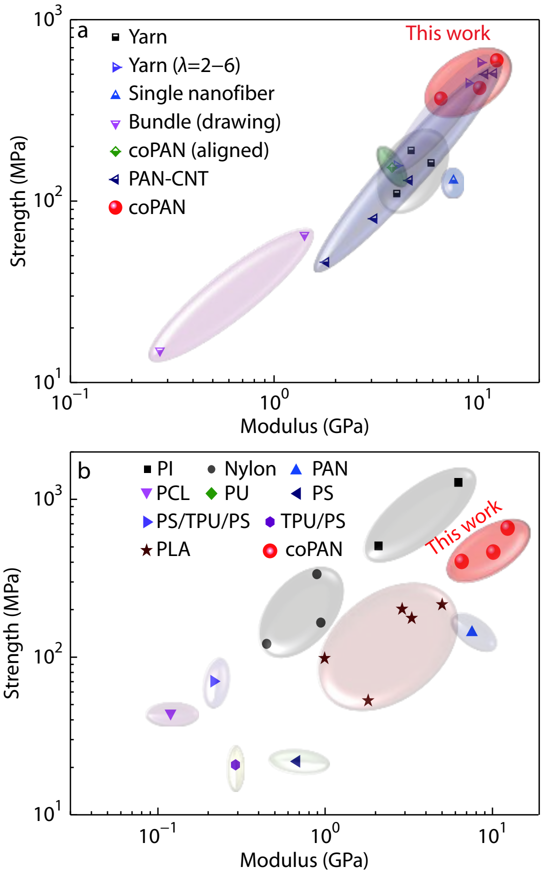

Fig. 6 Ashby plots of strength versus modulus of electrospun PAN-based materials (a) and other electrospun single fiber (b). Yarn,[46,47] PAN-CNT,[21,50–52] single nanofiber,[48] bundle (drawing),[49] coPAN (aligned),[36] yarn (λ=2–6),[37] PI,[57] Nylon,[53,54] PAN,[26] PCL,[55] TPU,[56] PS,[56] PS/TPU/PS triaxial,[56] TPU/PS core/shell,[56] and coPAN (this work).

CONCLUSIONS

Electrospun coPAN single nanofibers with different drawing times were successfully prepared by copolymerization, electrospinning and mechanical drawing. The diameter of the single nanofibers decreased as the drawing times increased, and the corresponding values agreed with the theoretical calculation. The results from polarized Raman spectroscopy confirmed that the electrospun coPAN single nanofiber possessed a degree of molecular orientation (P) of 0.656. After drawing to 2.2 times, the P values significantly increased to 0.808. The stretched single coPAN electrospun nanofibers with drawing times in the range of 1.4–2.2 had excellent mechanical properties with tensile strength of 367–595 MPa and modulus of 6.6–12.4 GPa. These properties of single coPAN nanofibers are much higher than those of most other electrospun PAN-based nanofiber yarns and bundles, and comparable to the yarns with drawing times of 2–6 and CNT reinforced PAN nanofibers.

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REFERENCES

1 Chand, S. Carbon fibers for composites. *J. Mater. Sci.* **2000**, *35*, 1303–1313.
2 Yusof, N.; Ismail, A. F. Post spinning and pyrolysis processes of polyacrylonitrile (PAN)-based carbon fiber and activated carbon fiber: a review. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 1–13.
3 Liu, Y.; Kumar, S. Recent progress in fabrication, structure, and properties of carbon fibers. *Polym. Rev.* **2012**, *52*, 234–258.
4 Hou, H.; Xu, W.; Ding, Y. The recent progress on high-performance polymer nanofibers by electrospinning. *Journal of Jiangxi Normal University (Natural Science)* (in Chinese) **2018**, *42*, 551–564.
5 Wei, J.; Liao, M.; Ma, A.; Chen, Y.; Duan, Z.; Hou, X.; Li, M.; Jiang, N.; Yu, J. Enhanced thermal conductivity of polydimethylsiloxane composites with carbon fiber. *Compos. Commun.* **2020**, *17*, 141–146.
6 Kobets, L.; Deev, I. Carbon fibres: structure and mechanical properties. *Compos. Sci. Technol.* **1998**, *57*, 1571–1580.
7 Paris, O.; Loidl, D.; Peterlik, H. Texture of PAN-and pitch-based carbon fibers. *Carbon* **2002**, *40*, 551–555.
8 Zeng, H. The development of carbon fibre and its composites in china. In *Proceedings of carbon fibres and their composites*, Berlin, Heidelberg, **1985**, pp. 288–293.
9 Duan, G.; Fang, H.; Huang, C.; Jiang, S.; Hou, H. Microstructures and mechanical properties of aligned electrospun carbon nanofibers from binary composites of polyacrylonitrile and polyamic acid. *J. Mater. Sci.* **2018**, *53*, 15096–15106.
10 Zhang, M. Y.; Niu, H. Q.; Qi, S. L.; Tian, G. F.; Wang, X. D.; Wu, D. Z. Structure evolutions involved in the carbonization of polyimide fibers with different chemical constitution. *Mater. Today Commun.* **2014**, *1*, 1–8.
11 Jiang, S.; Cheong, J. Y.; Nam, J. S.; Kim, I. D.; Agarwal, S.; Greiner, A. High-density fibrous polyimide sponges with superior mechanical and thermal properties. *ACS Appl. Mater. Interfaces* **2020**, *12*, 19006–19014.
12 Jiang, S.; Uch, B.; Agarwal, S.; Greiner, A. Ultralight, thermally insulating, compressible polyimide fiber assembled sponges. *ACS Appl. Mater. Interfaces* **2017**, *9*, 32308–32315.
13 Bermudez, V.; Ogale, A. A. Adverse effect of mesophase pitch draw-down ratio on carbon fiber strength. *Carbon* **2020**, *168*, 328–336.
14 Li, W. W.; Kang, H. L.; Xu, J.; Liu, R. G. Effects of ultra-high temperature treatment on the microstructure of carbon fibers. *Chinese J. Polym. Sci.* **2017**, *35*, 764–772.
15 Deng, L.; Young, R. J.; Kinloch, I. A.; Zhu, Y.; Eichhorn, S. J. Carbon nanofibres produced from electrospun cellulose nanofibres. *Carbon* **2013**, *58*, 66–75.
16 Ma, L.; Zhang, Y.; Wang, S. Modified treatment for carbonized cellulose nanofiber application in composites. *Compos. Part A* **2016**, *90*, 786–793.
17 Tian, J.; Shi, Y.; Fan, W.; Liu, T. Ditungsten carbide nanoparticles embedded in electrospun carbon nanofiber membranes as flexible and high-performance supercapacitor electrodes. *Compos. Commun.* **2019**, *12*, 21–25.
18 Weng, W.; Kurihara, R.; Wang, J.; Shiratori, S. Electrospun carbon nanofiber-based composites for lithium-ion batteries: structure optimization towards high performance. *Compos. Commun.* **2019**, *15*, 135–148.

19 Wu, Q. Y.; Liang, H. Q.; Li, M.; Liu, B. T.; Xu, Z. K. Hierarchically porous carbon membranes derived from PAN and their selective adsorption of organic dyes. *Chinese J. Polym. Sci.* **2016**, *34*, 23–33.

20 Santos de Oliveira Junior, M.; Manzolli Rodrigues, B. V.; Marcuzzo, J. S.; Guerrini, L. M.; Baldan, M. R.; Rezende, M. C. A statistical approach to evaluate the oxidative process of electrospun polyacrylonitrile ultrathin fibers. *J. Appl. Polym. Sci.* **2017**, *134*, 45458.

21 Hou, X.; Yang, X.; Zhang, L.; Waclawik, E.; Wu, S. Stretching-induced crystallinity and orientation to improve the mechanical properties of electrospun PAN nanocomposites. *Mater. Des.* **2010**, *31*, 1726–1730.

22 Baseri, S. Preparation and characterization of conductive and antibacterial polyacrylonitrile terpolymer yarns produced by one-step organic coating. *J. Text. Instit.* **2017**, *108*, 20–29.

23 Yao, K.; Chen, J.; Li, P.; Duan, G.; Hou, H. Robust strong electrospun polyimide composite nanofibers from a ternary polyamic acid blend. *Compos. Commun.* **2019**, *15*, 92–95.

24 Zhou, Z.; Liu, K.; Lai, C.; Zhang, L.; Li, J.; Hou, H.; Reneker, D. H.; Fong, H. Graphitic carbon nanofibers developed from bundles of aligned electrospun polyacrylonitrile nanofibers containing phosphoric acid. *Polymer* **2010**, *51*, 2360–2367.

25 Kaur, N.; Kumar, V.; Dhakate, S. R. Synthesis and characterization of multiwalled CNT-PAN based composite carbon nanofibers *via* electrospinning. *SpringerPlus* **2016**, *5*, 483.

26 Papkov, D.; Zou, Y.; Andalib, M. N.; Goponenko, A.; Cheng, S. Z. D.; Dzenis, Y. A. Simultaneously strong and tough ultrafine continuous nanofibers. *ACS Nano* **2013**, *7*, 3324–3331.

27 Jiang, S.; Chen, Y.; Duan, G.; Mei, C.; Greiner, A.; Agarwal, S. Electrospun nanofiber reinforced composites: a review. *Polym. Chem.* **2018**, *9*, 2685–2720.

28 Liu, L.; Bakhshi, H.; Jiang, S.; Schmalz, H.; Agarwal, S. Composite polymeric membranes with directionally embedded fibers for controlled dual actuation. *Macromol. Rapid Commun.* **2018**, *39*, 1800082.

29 Sun, Z.; Yang, L.; Zhang, D.; Song, W. High performance, flexible and renewable nano-biocomposite artificial muscle based on mesoporous cellulose/ionic liquid electrolyte membrane. *Sensors Actuators B: Chem.* **2019**, *283*, 579–589.

30 Jiang, S.; Helfricht, N.; Papastavrou, G.; Greiner, A.; Agarwal, S. Low-density self-assembled poly(*N*-isopropyl acrylamide) sponges with ultrahigh and extremely fast water uptake and release. *Macromol. Rapid Commun.* **2018**, *39*, 1700838.

31 Jian, S.; Zhu, J.; Jiang, S.; Chen, S.; Fang, H.; Song, Y.; Duan, G.; Zhang, Y.; Hou, H. Nanofibers with diameter below one nanometer from electrospinning. *RSC Adv.* **2018**, *8*, 4794–4802.

32 Jiang, S.; Agarwal, S.; Greiner, A. Low-density open cellular sponges as functional materials. *Angew. Chem. Int. Ed.* **2017**, *56*, 15520–15538.

33 Agarwal, S.; Jiang, S.; Chen, Y. Progress in the field of water- and/or temperature-triggered polymer actuators. *Macromol. Mater. Eng.* **2019**, *304*, 1800548.

34 Molnar, K.; Jedlovszky-Hajdu, A.; Zrinyi, M.; Jiang, S.; Agarwal, S. Poly(amino acid)-based gel fibers with pH responsivity by coaxial reactive electrospinning. *Macromol. Rapid Commun.* **2017**, *38*, 1700147.

35 Li, Y.; Yin, X.; Yu, J.; Ding, B. Electrospun nanofibers for high-performance air filtration. *Compos. Commun.* **2019**, *15*, 6–19.

36 Duan, G.; Liu, S.; Hou, H. Synthesis of polyacrylonitrile and mechanical properties of its electrospun nanofibers. *e-Polymer* **2018**, *18*, 569–573.

37 Liao, X.; Dulle, M.; de Souza e Silva, J. M.; Wehrspohn, R. B.; Agarwal, S.; Förster, S.; Hou, H.; Smith, P.; Greiner, A. High strength in combination with high toughness in robust and sustainable polymeric materials. *Science* **2019**, *366*, 1376–1379.

38 Zeng, Z. P.; Shao, Z. C.; Xiao, R.; Lu, Y. G. Structure evolution mechanism of poly(acrylonitrile/itaconic acid/acrylamide) during thermal oxidative stabilization process. *Chinese J. Polym. Sci.* **2017**, *35*, 1020–1034.

39 Duan, G.; Zhang, H.; Jiang, S.; Xie, M.; Peng, X.; Chen, S.; Hanif, M.; Hou, H. Modification of precursor polymer using co-polymerization: a good way to high performance electrospun carbon nanofiber bundles. *Mater. Lett.* **2014**, *122*, 178–181.

40 Kim, C.; Park, S. H.; Cho, J. I.; Lee, D. Y.; Park, T. J.; Lee, W. J.; Yang, K. S. Raman spectroscopic evaluation of polyacrylonitrile-based carbon nanofibers prepared by electrospinning. *J. Raman Spectrosc.* **2004**, *35*, 928–933.

41 Huang, Y. S.; Koenig, J. L. Raman spectra of polyacrylonitrile. *Appl. Spectrosc.* **1971**, *25*, 620–622.

42 Wang, D.; Yu, J.; Duan, G.; Liu, K.; Hou, H. Electrospun polyimide nonwovens with enhanced mechanical and thermal properties by addition of trace plasticizer. *J. Mater. Sci.* **2020**, *55*, 5667–5679.

43 Xu, H.; Jiang, S.; Ding, C.; Zhu, Y.; Li, J.; Hou, H. High strength and high breaking load of single electrospun polyimide microfiber from water soluble precursor. *Mater. Lett.* **2017**, *201*, 82–84.

44 Yang, H.; Jiang, S.; Fang, H.; Hu, X.; Duan, G.; Hou, H. Molecular orientation in aligned electrospun polyimide nanofibers by polarized FTIR spectroscopy. *Spectrochimica Acta Part A* **2018**, *200*, 339–344.

45 Jiang, S.; Han, D.; Huang, C.; Duan, G.; Hou, H. Temperature-induced molecular orientation and mechanical properties of single electrospun polyimide nanofiber. *Mater. Lett.* **2018**, *216*, 81–83.

46 Fennessey, S. F.; Farris, R. J. Fabrication of aligned and molecularly oriented electrospun polyacrylonitrile nanofibers and the mechanical behavior of their twisted yarns. *Polymer* **2004**, *45*, 4217–4225.

47 Yan, H.; Liu, L.; Zhang, Z. Continually fabricating staple yarns with aligned electrospun polyacrylonitrile nanofibers. *Mater. Lett.* **2011**, *65*, 2419–2421.

48 Naraghi, M.; Chasiotis, I.; Kahn, H.; Wen, Y.; Dzenis, Y. Mechanical deformation and failure of electrospun polyacrylonitrile nanofibers as a function of strain rate. *Appl. Phys. Lett.* **2007**, *91*, 151901.

49 Lai, C.; Zhong, G.; Yue, Z.; Chen, G.; Zhang, L.; Vakili, A.; Wang, Y.; Zhu, L.; Liu, J.; Fong, H. Investigation of post-spinning stretching process on morphological, structural, and mechanical properties of electrospun polyacrylonitrile copolymer nanofibers. *Polymer* **2011**, *52*, 519–528.

50 Hou, H.; Ge, J. J.; Zeng, J.; Li, Q.; Reneker, D. H.; Greiner, A.; Cheng, S. Z. D. Electrospun polyacrylonitrile nanofibers containing a high concentration of well-aligned multiwall carbon nanotubes. *Chem. Mater.* **2005**, *17*, 967–973.

51 Cai, J.; Chawla, S.; Naraghi, M. Microstructural evolution and mechanics of hot-drawn CNT-reinforced polymeric nanofibers. *Carbon* **2016**, *109*, 813–822.

52 Li, Y.; Góra, A.; Anariba, F.; Baji, A. Enhanced tensile strength and electrical conductivity of electrospun polyacrylonitrile yarns *via* post-treatment. *Polym. Compos.* **2019**, *40*, 1702–1707.

53 Bazbouz, M. B.; Stylios, G. K. The tensile properties of electrospun nylon 6 single nanofibers. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *48*, 1719–1731.

54 Zussman, E.; Burman, M.; Yarin, A. L.; Khalfin, R.; Cohen, Y. Tensile deformation of electrospun nylon-6,6 nanofibers. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1482–1489.

55 Tan, E. P. S.; Ng, S. Y.; Lim, C. T. Tensile testing of a single ultrafine polymeric fiber. *Biomaterials* **2005**, *26*, 1453–1456.

56 Jiang, S.; Duan, G.; Zussman, E.; Greiner, A.; Agarwal, S. Highly flexible and tough concentric triaxial polystyrene fibers. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5918–5923.

57 Chen, L.; Jiang, S.; Chen, J.; Chen, F.; He, Y.; Zhu, Y.; Hou, H. Single electrospun nanofiber and aligned nanofiber belts from copolyimide containing pyrimidine units. *New J. Chem.* **2015**, *39*, 8956–8963.