

# Effect of Diameter on the Structural Evolution and Tensile Properties of Electrospun PAN-Based Carbon Nanofiber Mats

Wei Zhang, Qian Sun, Zhigang Shen,\* Jie liu, and Xiaoxu Wang\*

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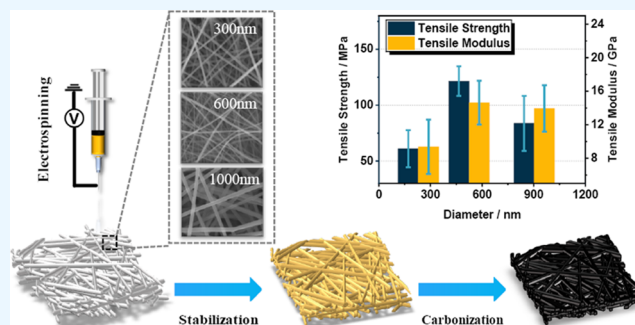


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**ABSTRACT:** The mechanical properties of carbon nanofiber mats (CNFMs) were closely correlated with the fiber diameter due to their brittle nature. In this work, CNFMs with different fiber diameters were prepared by electrospinning with different spinning parameters, followed by stabilization in air and carbonization in nitrogen. Structural characterizations revealed that PAN nanofibers with smaller diameters tended to form larger cross-linking structures during stabilization. Meanwhile, the degree of graphitization of CNFMs was higher when the diameter was reduced. However, the tensile properties of CNFM were not solely determined by the fiber diameter but were the general reflection of structural regularity and defects. The highest tensile strength of 125.2 MPa was achieved when the fiber diameter was around 500 nm.



## 1. INTRODUCTION

Carbon nanofiber mats (CNFMs) have been studied in fundamental and applied research fields due to their great potential in many fields, such as electrode materials for batteries, supercapacitors, and catalytic reactors.<sup>1–10</sup> Many alternative precursors have been used to produce CNFMs, such as polyacrylonitrile (PAN), cellulose, polyimide (PI), pitch, poly(vinyl alcohol) (PVA), and poly(methyl methacrylate) (PMMA). PAN is a popular precursor material for preparing CNFMs owing to its advantages of being environmentally friendly, easy dehydrocyclization, high pyrolysis speed, and high carbon yield. However, the poor mechanical properties restrict the wider applications of CNFMs.<sup>11–13</sup> Therefore, it is desirable to understand the mechanism of preparing PAN-based high-strength CNFMs.

Carbon fiber is brittle, and its tensile properties are largely determined by the presence of defects. The effect of defects can be limited by reducing the cross-sectional area. As a result, it is well known that commercial carbon fibers could increase their mechanical properties by reducing the diameter of the fibers, namely, the size effect.<sup>14,15</sup> CNFMs and commercial carbon fibers both use PAN as the precursor; they also have similar crystalline structures.<sup>6,14,16,17</sup> The tensile strength of single-carbon nanofibers is comparable to commercial carbon fibers, as mentioned in the literature.<sup>18</sup> Therefore, it is reasonable to propose that the mechanical properties of CNFMs can be increased by reducing the diameter of carbon nanofibers.

In this paper, three types of PAN nanofiber mats with diameters in the range of 300–1000 nm were obtained by controlling the electrospinning parameters. After the stabiliza-

tion and carbonization processes, three types of CNFMs with different diameters were obtained. The structural evolution of CNFMs with different diameters was characterized, and the relationship between the structures and the tensile properties of CNFMs was discussed.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Methods.** *N,N*-Dimethylformamide (DMF) was provided by Acros Ltd. Polyacrylonitrile (PAN) ( $M_w = 150,000$  g/mol) was provided by Courtaulds Ltd. All chemicals were used as received.

The spinning parameters were as follows: high voltage 12–20 kV, electrode–substrate distance 13–25 cm, relative humidity 25%, and temperature 24.0 °C. The spinning solution contained 8–14% PAN dissolved in DMF. During stabilization, PAN nanofiber mats were placed in a preheated oven through the top window and were kept at 215–230–245–260 °C for 20 min. For carbonization, the stabilization nanofiber mats were heated from room temperature to 1300 °C with a heating rate of 5 °C per minute in a tube furnace under a nitrogen atmosphere.<sup>19</sup>

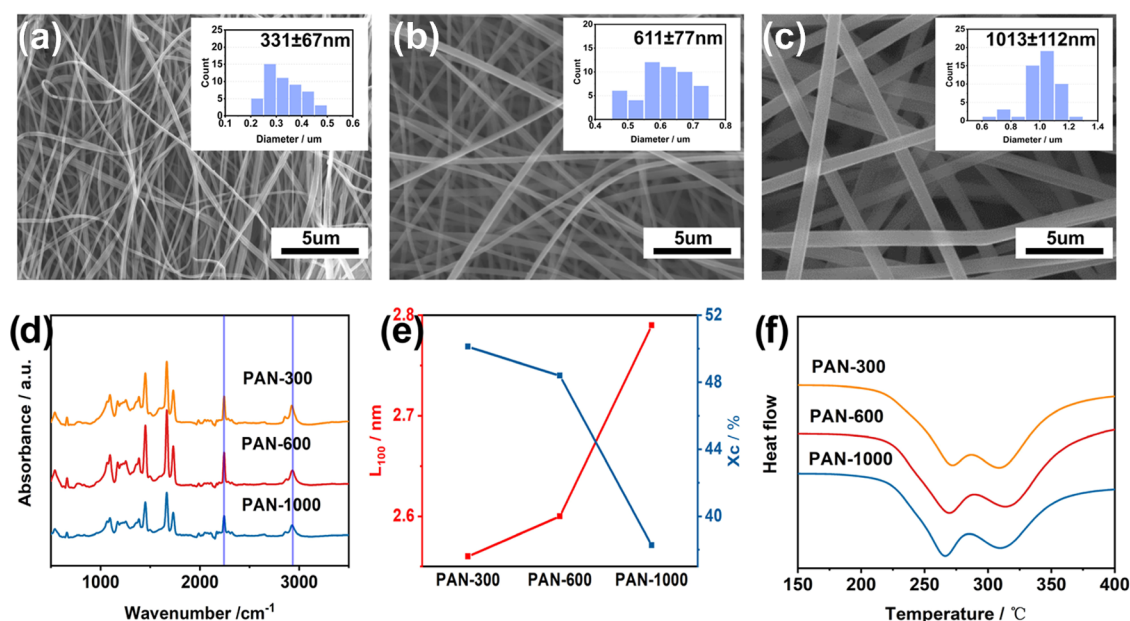
**2.2. Characterization.** The chemical structures were characterized by a Fourier transform infrared (FT-IR)

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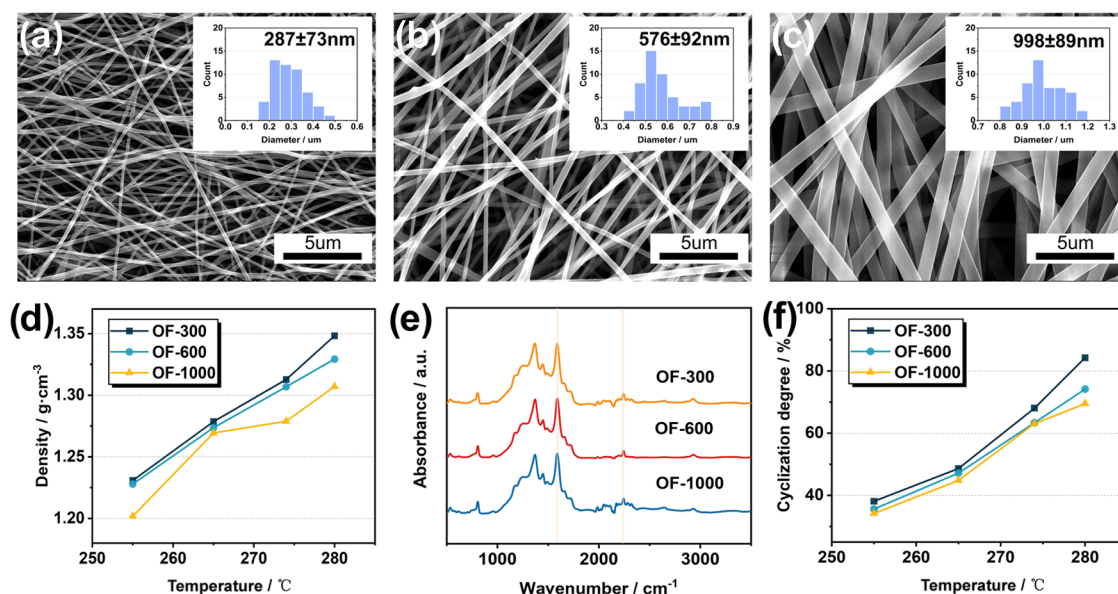
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**Figure 1.** SEM images of (a) PAN-300, (b) PAN-600, and (c) PAN-1000 with insets showing the diameter distribution of PAN nanofiber mats; (d) FT-IR spectrum; (e) degree of crystallinity ( $X_c$ ) and the crystalline size ( $L_{100}$ ), and (f) DSC of PAN nanofiber mats with different diameters.



**Figure 2.** SEM images of (a) OF-300, (b) OF-600, and (c) OF-1000, with insets showing diameter distribution; (d) density of stabilization nanofiber mats under different temperatures; (e) FT-IR spectrums of stabilization nanofiber mats with different diameters; and (f) degree of cyclization of stabilization nanofiber mats under different temperatures.

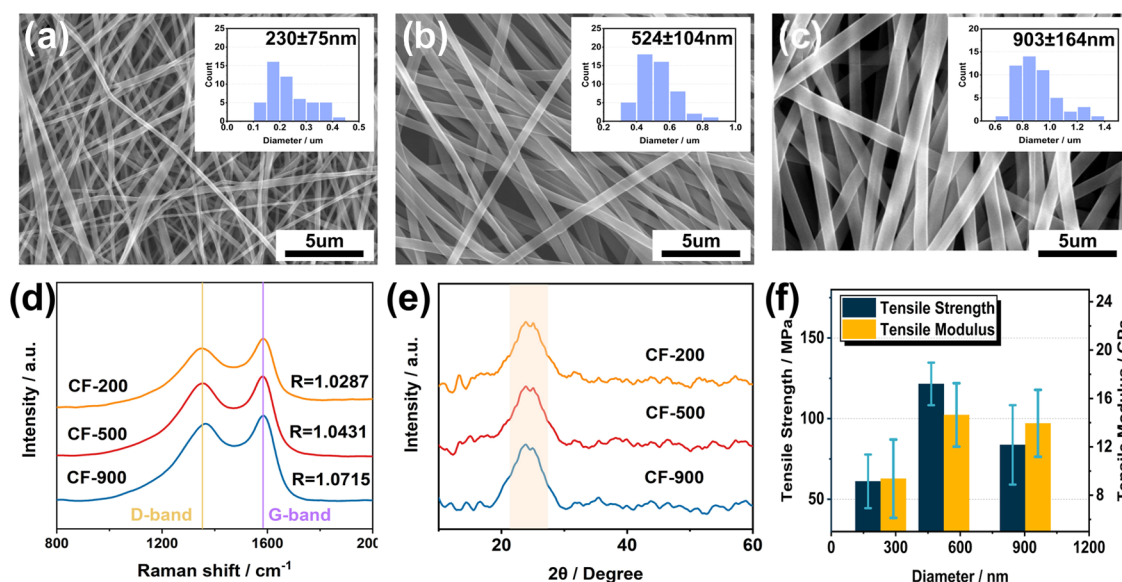
spectrometer in the wavenumber range of 500–4000  $\text{cm}^{-1}$ . Scanning electron microscopy (SEM) measurements were implemented on a Hitachi S-4700. Raman spectra of the CNFMs were taken with a Renishaw RM 200 (514.5 nm excitation and a notch filter between 500 and 2400  $\text{cm}^{-1}$ ). Differential scanning calorimetry was conducted on a METTLER 1/400Pro at a heating rate of 5  $^{\circ}\text{C}$  per minute from 30 to 400  $^{\circ}\text{C}$ . The X-ray diffraction (XRD) tests were performed on a Bruker D8 Advance X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm) in a  $2\theta$  angle range of 5–60 $^{\circ}$ . A DC-02 density gradient column was used to test the density of the mats. Tensile tests of the CNFMs were conducted by an INSTRON-5578. The speed was 5 mm/min, and 10 samples

with lengths of 40 mm and widths of 5 mm were prepared for each tensile test.

### 3. RESULTS AND DISCUSSION

The SEM images of (a), (b), and (c) in Figure 1 show the representative morphologies of PAN. The fiber diameters of 331  $\pm$  67, 611  $\pm$  77, and 1013  $\pm$  112 nm are denoted as PAN-300, PAN-600, and PAN-1000, respectively. As shown in Figure 1d, the FT-IR spectrum indicates that the differences in the diameter have no obvious effect on the chemical structure of PAN nanofiber mats.

It is worth noting that the size of the spinning orifices is identical for all three samples; smaller fiber diameters indicate that the fiber experienced a high degree of drawing during



**Figure 3.** SEM images of (a) CF-200, (b) CF-500, and (c) CF-900, with insets showing the diameter distribution of CNFMs; (d) Raman spectrums of CNFMs; (e) XRD patterns; and (f) tensile strength and tensile modulus of CNFMs with different diameters.

electrospinning, leading to a higher degree of crystallinity. As shown in Figure 1e,  $X_c$  decreases with increasing diameter, whereas  $L_{100}$  increases with increasing diameter.

In addition, PAN nanofiber mats with smaller diameters have lower initiation temperatures for the oxidation reaction, as shown in Figure 1f. PAN nanofiber mats with smaller diameters have a larger specific surface area and a smaller crystallite size, as shown in Table S2, which is beneficial for the diffusion of oxygen during stabilization.

The thermo-oxidative stabilization process is an important intermediate process in the production of CNFMs. Figure 2a–c shows the representative morphologies of stabilized nanofiber mats with different diameters. All samples experience a small amount of shrinkage in the diameter after stabilization, but there is no obvious change in the fiber morphology. FT-IR is used to characterize the chemical functional group change of CNFMs, as shown in Figure 2e. The 1590 and 2240  $\text{cm}^{-1}$  peaks are associated with the adsorption of the C=N and C≡N groups, respectively. The intensity of the C=N group and the C≡N group is used to calculate the degree of cyclization, as shown in Figure 2f. It can be seen that decreasing the fiber diameter effectively improves the degree of cyclization. With the decrease in fiber diameter, the oxygen element can diffuse more readily into the fibers and facilitate the cyclization reaction. Density analysis is widely used in the production of carbon fibers. Density is a macroscopic representation of the physical and chemical structure of the CNFMs. The density shows the same trend as the degree of cyclization, as shown in Figures 2d and S4.

The SEM images of (a), (b), and (c) in Figure 3 show the representative morphologies of CNFMs. The fiber diameters of  $230 \pm 75$ ,  $524 \pm 104$ , and  $903 \pm 164$  nm are denoted as CF-200, CF-500, and CF-900, respectively. The fiber diameter noticeably decreased after carbonization, which is attributed to the removal of non-carbon elements, as shown in Figure S5.

As shown in Figure 3d, Raman spectroscopy measurements show a higher  $I_D/I_G$  ratio in CF-900 compared to CF-200. The higher  $I_D/I_G$  value also suggests a higher degree of disorder and defect in CF-900.

Furthermore, the XRD patterns show that all three samples exhibit diffraction peaks at  $24.5^\circ$  corresponding to the (002) plane of graphite, as shown in Figure 3e. With the increase in diameter, the interlayer spacing increases from 0.36 to 0.37 nm, and the stack thickness decreases from 0.78 nm to 0.73 nm. These results indicate that a smaller diameter is in favor of the growth of graphite crystallites during carbonization.

CNFMs with the highest tensile strength and modulus are obtained when the diameters of CNFMs are around 500 nm. Further increasing or decreasing the diameters reduces tensile properties, as shown in Figure 3f. Ideally, CNFMs with a smaller diameter would have better tensile properties since they possess a higher degree of graphitization and a lower amount of defects. Previous studies have revealed that surface energy plays an increasingly important role when fiber diameters decrease to the nanometer scale.<sup>19</sup> Nanofibers demonstrate a strong tendency to adhere to each other due to high surface energy, and the adhesion is pronounced in CF-200, as shown in Figures S7–S9. The adhesion of fibers facilitates the propagation of cracks during the brittle fracture of CNFMs. Consequently, the tensile properties of CF-200 deteriorate.

#### 4. CONCLUSIONS

In conclusion, the diameter greatly influences the structural evolution and the tensile properties of CNFMs. PAN nanofiber mats with smaller diameters have a higher degree of crystallinity and lower initiation temperature of the oxidation reaction. During the thermo-oxidative stabilization process, the mats with smaller diameters have a larger specific surface area, more oxygen uptake, and a higher degree of cyclization. After the carbonization, CNFMs with smaller diameters have a higher degree of graphitization and a larger crystalline size. The tensile properties of CNFMs are influenced by the fibers' microstructure and the mats' structural integrity. The adhesion of nanofibers becomes pronounced with decreasing fiber diameters and therefore deteriorates the tensile properties of CF-200. CNFMs with the highest tensile strength are obtained when the fiber diameter is around 500 nm.



## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c01708>.

XRD, SSA, and DSC of PAN nanofibers; density, NMR, XPS, and FT-IR of stabilization nanofibers; and Raman, tensile properties, and XRD of CNFMs (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Zhigang Shen** – SINOPEC Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China; Email: [shenzg.sshy@sinopec.com](mailto:shenzg.sshy@sinopec.com)

**Xiaoxu Wang** – Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China; Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, Jiangsu 213164, China; [orcid.org/0000-0003-4649-4483](https://orcid.org/0000-0003-4649-4483); Email: [wangxiaoxu@mail.buct.edu.cn](mailto:wangxiaoxu@mail.buct.edu.cn)

### Authors

**Wei Zhang** – Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

**Qian Sun** – Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

**Jie liu** – Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, Jiangsu 213164, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.3c01708>

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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