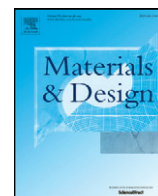Effect of carbonization temperature on properties of aligned electrospun
polyacrylonitrile carbon nanofibers
Liu C.-K., Feng Y., He H., Zhang J., Sun R.-J., Chen M.-Y.

Effect of carbonization temperature on properties of aligned electrospun polyacrylonitrile carbon nanofibers

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ABSTRACT

Aligned electrospun nanofibrous bundle was used as the raw material for pretreatment, preoxidation and carbonization processes to prepare carbon nanofibers in a procedure temperature-controlled sintering furnace. Effect of carbonization temperature on the morphology and structural performance of nanofibers was investigated in present study. Results showed that R_I (the relative intensity radio between Disordered peak and Graphite peak) of nanofibers carbonized at 1000 °C is 0.90, carbon content is up to 85.67%, conductivity is 105.44 S·cm^{-1}, Young's modulus is 68.8 ± 0.42 GPa, and fiber strength is 306.0 ± 9.0 MPa, all of which endow the fibers with a superior comprehensive property.

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1. Introduction

Carbon nanofiber can be applied in many fields including reinforcing materials, template for the preparation of nanotubes, high-temperature filter, and high-temperature catalytic matrix materials due to its superior properties, such as high specific surface area, high temperature resistance, and good electrical/thermal conductivity [1]. Traditional preparation methods of carbon nanofiber include support catalyst method, spraying method, vapor grown method, and so on. However, these methods are relatively complicated and high-cost. Therefore, a simple and relatively cheap electrospinning process, without the requirement of purification process, is gradually regarded as the optimum process for the preparation of continuous and uniform carbon nanofibers. Carbon nanofibers prepared by precursors, such as polyacrylonitrile (PAN) [2–12], pitch [13], polybenzimidazole [14], and polyimide [15,16], have been reported in the existing literature. Among them PAN is mainly used to prepare carbon nanofibers through electrospinning process because of its high carbonization rate and simple carbonization process. Aligned electrospun PAN nanofiber bundle has been used as precursor fibers, which were pretreated by washing, drying densification, and damp-heat drafting, to prepare preoxidized nanofibers with relatively good properties in our former research [17–19]. Based on this, effect of heat treatment temperature on the morphology and structural performance of carbon nanofibers was further investigated in this article.

2. Experimental

2.1. Materials and apparatuses

PAN ($M_W = 100,000$ g·mol^{-1}) was purchased from Shanxi Hengtian New Textile Fiber Tech, China. N,N-dimethylformamide (DMF) was obtained from Tianjin Fuyu Fine Chemical Industry, China, which was used directly without further purification.

The vertical electrospinning set-up, which mainly consisted of a DC high-voltage generator (Chengdu Chuangao Electric Technology Co., Ltd.) and a micro-injection pump (Zhejiang University Medical Instrument Co., Ltd.), was used to prepare nanofibers. The magnetic stirrer (Hangzhou Instrument Motor Co., Ltd.) was selected in the preparation of spinning solution. The procedure temperature-controlled sintering furnace, which has been described in our published document, was homemade [19].

2.2. Methods

The selected electrospinning parameters were as follows: PAN was dissolved in DMF to prepare the solution with the concentration of 15 wt.%; flow rate was 0.3 mL·h^{-1}; applied voltage was 12 kV; distance between the needle tip and the collector was 12 cm; the collector was plane aluminum plate; collecting time was 40 min; and environmental temperature and relative humidity were 19 ± 2 °C and 45 ± 5 RH%,

respectively. The aligned nanofibers were treated through the following steps: washing, drying densification, and fourfold damp-heat drafting to prepare precursor fibers. The prepared fibers were used to prepare preoxidized nanofibers with heat treatment temperature at 283 °C for 1 h and subsequent carbon nanofibers through low-temperature carbonization. The carbonization temperatures were selected as 400 °C, 700 °C and 1000 °C respectively with the heating rate of 5 °C·min^{-1}. The effect of heat treatment temperature on the morphology and structural performance of carbon nanofibers was studied. The fiber might shrink in the carbonization process, leading to the formation of the micro-pits on the surface of fiber, which will deteriorate the properties of fiber. So the tension was selected as 0.02 cN·dtex^{-1} in this article, which must be exerted on the fiber in the carbonization process to keep and optimize the orientation structure formed in the preoxidized process.

2.3. Measurements

The changes of molecular structure were measured by Fourier transform infrared spectroscopy (Vertex 70, Bruker) with the KBr pressed-disk technique. The scanning range was 400–4000 cm^{-1}, and 256 scans with a spectral resolution 4 cm^{-1} were selected during each measurement. Raman spectroscopy (InVia, Renishaw) was used to obtain the Raman spectrum of carbon fiber with a scanning range of 200–
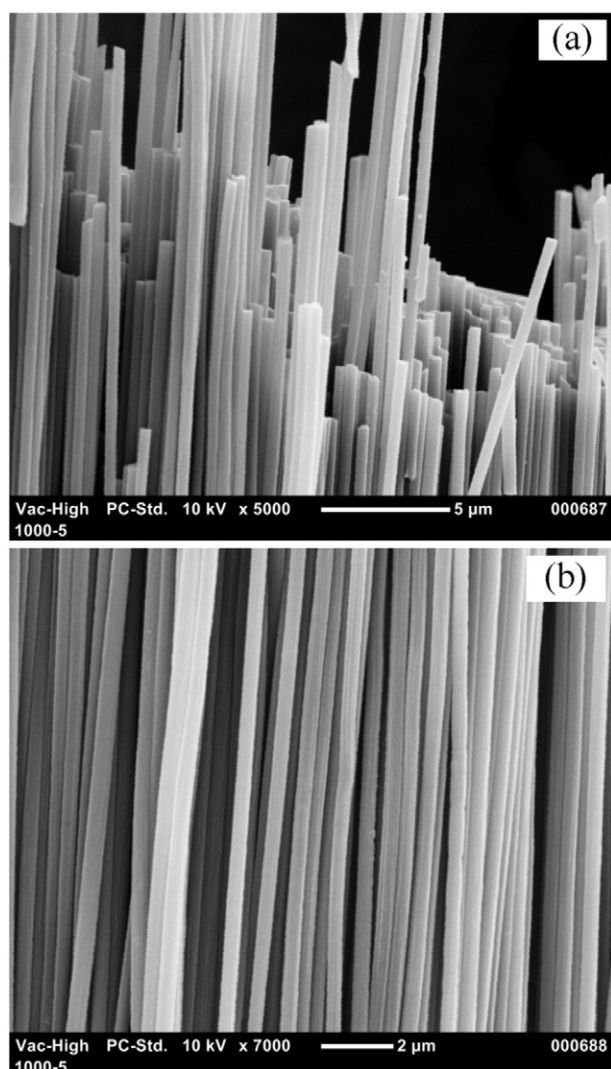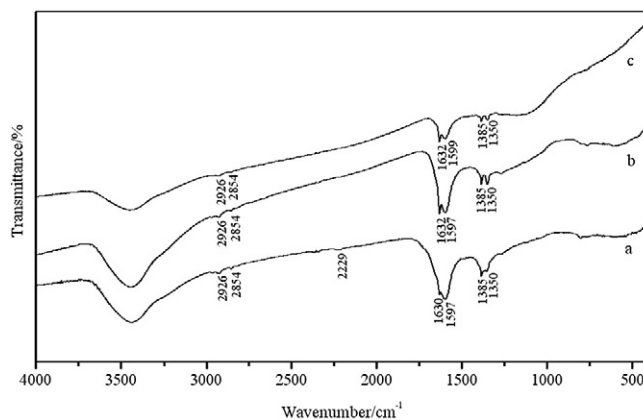

Fig. 2. FTIR curves of fibers carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

2000 cm^{-1}. The scanning speed was 10 s with 3 superpositions. The wave length was 514.5 nm and power was 20 mW attenuated to 10%. The changes of element content in the carbonization process were obtained by an element analyzer (Vario EL III, Elementor). Appearance of fibers was characterized by a scanning electron microscope (Vega II, Tescan). Electrical conductivity of fiber was measured by an electrical conductivity meter (Fluke). Mechanical properties of fiber was measured using a strength tester (5565, Instron).

3. Results and discussion

3.1. Effect of carbonization temperature on morphology of nanofibers

Fig. 1 shows the SEM photos of the fibrous bundle carbonized at 1000 °C. It is obvious that the fibers do not adhere to each other and being well even-distributed. The diameter of fiber (380 ± 30 nm) after preoxidation and carbonization processes is thinner than the diameter of precursor fiber (410 ± 28 nm) treated by fourfold damp-heat drafting because of the structural change, weight loss of fiber, and the tension exerted on the fiber in the pre-oxidation and carbonization processes. Non-carbon elements are removed through structure rearrangement of PAN preoxidized nanofiber, condensation and polymerization of cyclized molecular chains, resulting in an increased
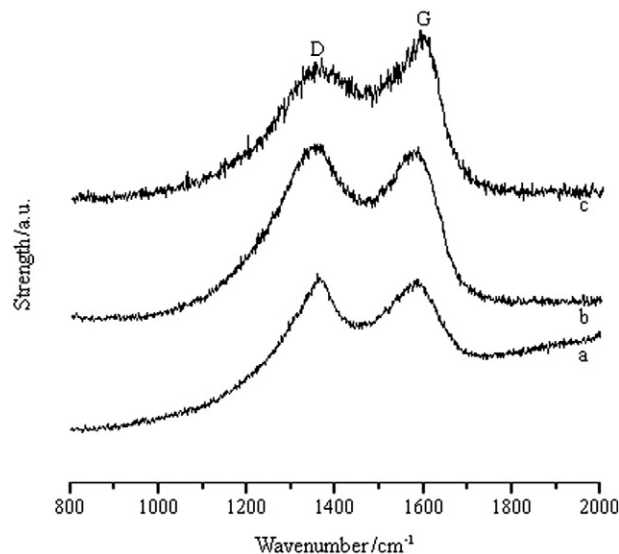

Fig. 1. SEM photos of the fibrous bundle carbonized at 1000 °C: (a) fracture morphology; and (b) surface state.

Fig. 3. Raman curves of fibers carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Table 1
Raman spectral parameters for nanofibers carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Carbonization temperatures/°C	D peak/cm^{-1}	G peak/cm^{-1}	R_I	L_a/nm
400	1360.7	1583.2	1.23	3.58
700	1363.8	1586.2	1.18	3.73
1000	1363.8	1586.2	0.90	4.89

Table 3
Conductivity for nanofibers carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Carbonization temperature/°C	Conductivity/S·cm^{-1}
400	0.015
700	0.018
1000	105.44

density of ladder structure and a formation of a flat sheet structure of carbon. With the increase of carbonization temperature, the distance between flat sheets of carbon is reduced, and a preferred arrangement of the flat sheets is induced along the fiber axis with the tension, which leads to a denser structure and a smaller diameter.

3.2. Effect of carbonization temperature on molecular structure

Fig. 2 shows the FTIR spectra of fibers carbonized at different temperatures. At temperature of 400 °C, a weak and small peak appearing at 2229 cm^{-1} proves that $-C\equiv N$ is still existed in the molecular structure, and when the temperature is increased to 700 °C or 1000 °C, $-C\equiv N$ disappears because of the increase of carbonization degree. The characteristic stretching vibration peaks at 1632 cm^{-1} and 1597 cm^{-1} belong to C=N, and the characteristic stretching vibration peaks at 1385 cm^{-1} and 1350 cm^{-1} belong to C–N. The characteristic stretching vibration peaks at 2926 cm^{-1} and 2852 cm^{-1} belong to C–H on $-CH_3$ and $-CH_2-$, respectively. When the carbonization temperature is 1000 °C, the characteristic peaks at 2926 cm^{-1}, 2852 cm^{-1}, 1385 cm^{-1} and 1350 cm^{-1} weaken significantly compared with those at 400 °C and 700 °C, which indicates that the number of C=N and C–N remarkably decrease, and more heteroaromatic rings transformed to graphite-like structure. The disappearance of the absorption band at 808 cm^{-1} assigning to C–H of heteroaromatic ring further demonstrate that more graphite-like structures have been formed.

3.3. Effect of carbonization temperature on degree of carbonization

Disordered peak (D peak) and Graphite peak (G peak) appear at around 1360 cm^{-1} and 1580 cm^{-1} at three different carbonization temperatures as shown in Fig. 3. D peak can characterize the disorder due to the incompletion of graphite microcrystal, the random arrangement of edge, and low symmetric carbon structure. G peak is the characteristic peak of graphite structure. So the relative intensity radio between D peak and G peak ($R_I = I_D/I_G$) can characterize the carbonization degree of carbon nanofibers. The smaller the value of R_I is, the higher the carbonization degree is. The surface microcrystal size of carbon fiber L_a can be determined by R_I, and the corresponding function is $L_a(nm) = 4.4/R_I$. Table 1 shows the value of R_I and L_a at three different carbonization temperatures. At 400 °C and 700 °C, $R_I > 1$ means the intensity of D peak is bigger than that of G peak, which indicates that the content of carbon in the graphite structure is relatively low in the carbon fiber. When the temperature is increased to 1000 °C, $R_I < 1$ means the intensity of G peak is bigger than that of D peak, and L_a is increased to 4.89 nm, which indicates that most of the carbon atoms exist in the form of graphite structure, and the microstructure tends to be in order.

Table 2
Contents of related elements for nanofibers carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Carbonization temperatures/°C	C/%	N/%	H/%	O/%
400	63.98	15.60	2.449	9.139
700	74.24	15.51	2.221	7.726
1000	85.67	6.765	1.054	2.825

3.4. Effect of carbonization temperature on contents of related elements

Table 2 shows contents of the related elements for nanofibers carbonized at different temperatures. It indicates that carbon content of carbonized nanofibers gradually increases with the increase of carbonization temperature. Results show that carbon content of nanofibers at the carbonization temperature of 1000 °C is 85.67%. With the carbonization temperature increased from 400 °C to 700 °C, only a small decrease of nitrogen and hydrogen contents. However, at the temperature of 1000 °C, they are significantly reduced to the half compared with the content at 700 °C. This confirms the results from Fig. 2. The number of C=N and C–N significantly decreases, and more aromatic heterocyclic ring structures have been changed to graphite-like structure when the carbonization temperature is 1000 °C.

3.5. Effect of carbonization temperature on conductivity of fibers

Table 3 presents the conductivity for nanofibers carbonized at different temperatures. As shown in the table, at 400 °C and 700 °C, the conductivities of fibers are 0.015 S·cm^{-1} and 0.018 S·cm^{-1}, respectively. The conductivity is significantly increased to 105.44 S·cm^{-1} when the temperature is up to 1000 °C. The reasons leading to this result can be explained from the following aspects: firstly, along the reaction process, fiber diameter is decreased as a result of the increase of specific surface area. Secondly, the preferred orientation of carbon layer with a flat structure increases significantly. Thirdly, cavity volume rate decreases effectively and crystallite dimension increases substantially. Fourthly, with the increase of treatment temperature, graphite-like band structure begins to change to a graphite-like flake structure during the reaction process of dehydrogenation and denitrification. With the further increase of temperature, the flake structures cohere together and orient along the longitudinal direction, which finally leads to a significant increase of conductivity. Therefore, carbon nanofibers carbonized at 1000 °C have possessed a sufficient carbonization degree and structural integrity.
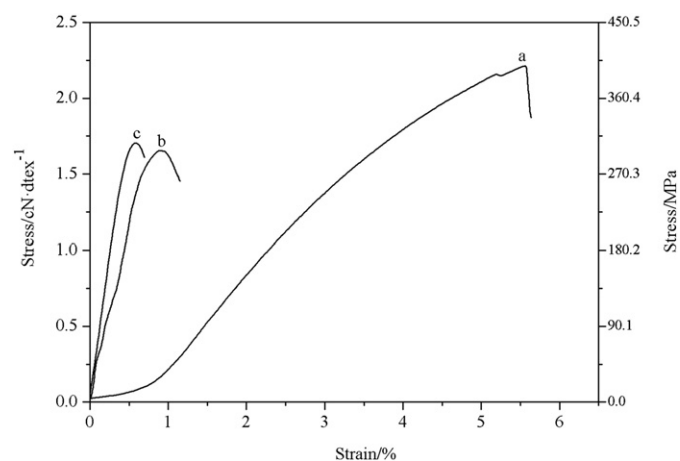

Fig. 4. Stress–strain curves of nanofibrous bundles carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Table 4
Mechanical properties of nanofibrous bundles carbonized at three different temperatures: (a) 400 °C; (b) 700 °C; and (c) 1000 °C.

Carbonization temperature/°C	Breaking strength/MPa	Elongation at break/%	Young's modulus/GPa	Specific work of rupture/J·g^{-1}
400	394.2 ± 5.4	5.57 ± 0.83	6.07 ± 0.23	6.65 ± 0.37
700	298.8 ± 3.6	0.91 ± 0.09	49.2 ± 0.33	1.29 ± 0.13
1000	306.0 ± 9.0	0.58 ± 0.05	68.8 ± 0.42	0.79 ± 0.15

3.6. Effect of carbonization temperature on mechanical properties of fibers

Fig. 4 shows the stress–strain curves of nanofibrous bundles carbonized at different temperatures. Specific performance parameters are shown in Table 4. It can be seen that yield zone disappears, and elongation at break and specific work of rupture both decrease significantly, while the Young's modulus increases remarkably after carbonization for nanofibrous bundles. When the carbonization temperature is 1000 °C, the elongation at break and the specific work of rupture are only 0.58 ± 0.05% and 0.79 ± 0.15 J·g^{-1}, respectively, while Young's modulus increases to 68.8 ± 0.42 GPa. Moreover, it can be found that tensile curve of carbon nanofiber gradually approaches to a straight line with the increase of carbonization temperature. This demonstrates that the tenacity of carbon nanofiber decreases, while stiffness increases significantly. However, when the carbonization temperature is 1000 °C, fiber strength is not high enough but show a slight decrease compared with precursor fibers. It might be attributed to the escape and volatilization of atoms except for carbon with the increase of heat treatment temperature, forming a certain number of holes on the fiber surface and inside. It may limit its application in reinforcing material of structure composite, but it is still a preferable candidate material for increasing electrical conductivity and thermal expansion coefficient.

4. Conclusions

Carbon nanofibers are prepared through preoxidation and carbonization processes in a procedure temperature-controlled sintering furnace. The value of R_I of nanofibers carbonized at 1000 °C is 0.90, carbon content is up to 85.67%, conductivity is 105.44 S·cm^{-1}, Young's modulus is 68.8 ± 0.42 GPa, and fiber strength is 306.0 ± 9.0 MPa, all of which endow the fibers with a superior comprehensive property. The prepared carbon nanofibers are expected to be applied in semiconductor manufacturing, electrostatic dissipation of the car's tank, high-temperature resistant catalyst carrier and high corrosive environment, and so on.

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