

## Effect of Temperature and Holding Time on Preoxidation for Aligned Electrospun Polyacrylonitrile Nanofibers

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**ABSTRACT:** In this article, aligned electrospun polyacrylonitrile nanofiber bundles were prepared as the precursor fibers to prepare preoxidized nanofibers through washing, drying densification, damp-heat drafting, and preoxidation process. Effects of preoxidation temperature and holding time on appearance and microstructure of the preoxidized fibers were studied. Fiber density is increased from 1.159 to 1.193 g cm<sup>-3</sup> after drying densification. Crystallinity is increased from 22.66 to 45.90% after fourfold drafting. The aligned preoxidized nanofibers were prepared at the optimum preoxidation temperature of 283°C, heating speed of 1°C min<sup>-1</sup>, and holding time of 1 h show a sufficient reaction degree of cyclization and crosslinking. Moreover, there is no occurrence of adhesion between fibers. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1158–1163, 2013

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### INTRODUCTION

Carbon nanofiber can be applied in many fields including reinforcing materials, template for the preparation of nanotubes, high-temperature filter, high-temperature catalytic matrix materials, and super capacitor because of its superior properties, such as high aspect ratio, high specific surface area, high temperature resistance, and good electrical/thermal conductivity.<sup>1</sup> Traditional preparation methods of carbon nanofiber include support catalyst method, spraying method, vapor grown method, and plasma enhanced chemical vapor deposition method. However, these methods are relatively complicated and high-cost. Therefore, a simple and relatively cheap electrospinning process is gradually regarded as the optimum process for the preparation of continuous carbon nanofibers with uniform diameter in last decade. Moreover, purification process is not required.

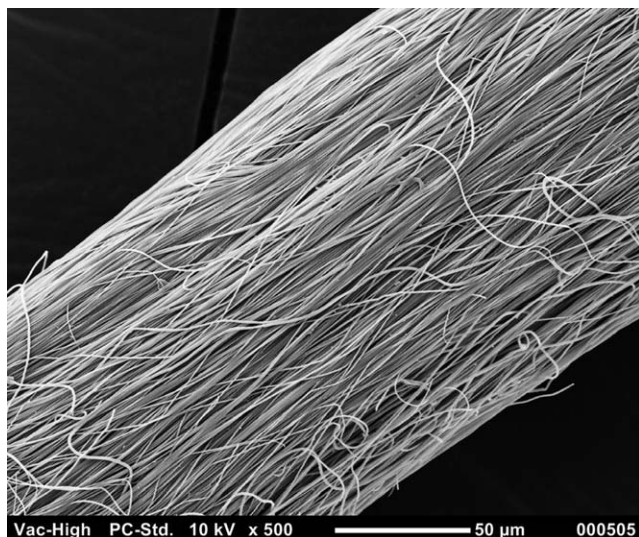
Polyacrylonitrile (PAN) is generally used to prepare carbon nanofibers through electrospinning process because of its high carbonization rate and simple carbonization process.<sup>2–16</sup> Carbon nanofibers made from other precursors, such as pitch, polyimide, and polybenzimidazole have also been reported.<sup>17–20</sup> However, existing literature has not comprehensively considered the following problems: residual solvent, compact degree, and

crystallinity of the electrospun nanofibers. In addition, for the fields such as microelectronics and composites reinforced by nanofibers, aligned nanofiber array would only have a giant application potential. Therefore, aligned electrospun PAN nanofiber bundle was used as precursor fibers, which were pretreated by washing, drying densification, and damp-heat drafting, to prepare preoxidized nanofibers in this article. Preoxidation is the most time-consuming process for the preparation of carbon nanofibers so as to ensure a sufficient reaction and make fibers not melt and burn during carbonization. So research on preoxidation is very essential for preparation of carbon nanofibers. Influences of preoxidation temperature and holding time on properties of preoxidized fibers were investigated.

### EXPERIMENTAL

#### Materials

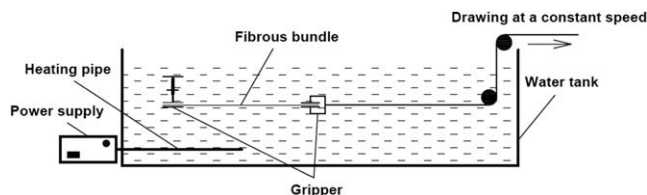
PAN fibers (Shanxi Hengtian New Textile Fiber Tech, China, precursor for carbon fibers,  $M_w = 100,000$  g mol<sup>-1</sup>) prepared through wet-spinning process was dissolved in *N,N*-dimethylformamide (DMF) (Tianjin Fuyu Fine Chemical Industry, China) to prepare uniform solution with the concentration of 15 wt %. All chemicals were used directly without further purification.



**Figure 1.** SEM image of nanofibrous bundle processed through fourfold drafting.

### Methods

A conventional vertical electrospinning set-up was used. The selected electrospinning parameters were as follows: voltage applied by a DC high-voltage generator was 12 kV; flow rate controlled by a micro-injection pump was 0.3 mL h<sup>-1</sup>; distance between the needle tip and the surface of electrically conducting plate was 12 cm; collecting device was plane aluminum plate; collecting time was 40 min; environmental temperature and relative humidity were 19 ± 2°C and 45 ± 5 RH%, respectively. The electrospinning jet with a minor whipping instability was found to rotate along the circumferential direction with a high speed (ca. 1500 r min<sup>-1</sup>). Therefore, the jet was easy to be stretched during high-speed rotation and formed aligned nanofiber assembly, which was then treated through washing, drying densification, and fourfold damp-heat drafting to prepare precursor fibers which are shown in Figure 1. The washing process was operated as follows: the aligned nanofiber bundle was clamped on both ends and dipped into a washing bath (40°C) for 30 min to make residual solvent be fully removed. After washing, the fibrous bundle was taken into a drying oven



**Figure 2.** Schematic of the damp-heat drafting setup.

(110°C) and hanged in a tension-free state for 4 min to conduct the drying densification. Damp-heat drafting (the corresponding set-up was presented in Figure 2) was carried out in a 97°C water bath with the drafting speed of 300 mm min<sup>-1</sup>, and the heat-stable time of 10 min.

Precursor nanofibers were preoxidized through a lab-made high-temperature sintering furnace tube as shown in Figure 3. Hot air was used to provide oxygen for preoxidation, and entrain reaction heat and byproducts to promote preoxidation. To ensure the preferred orientation of fiber macromolecules, an appropriate tension should be applied to adapt to the physico-chemical changes and structure transformation. It was reported that the tension could be in the range of 0.04 and 0.26 cN dtex<sup>-1</sup>. The tension during preoxidation was selected as 0.04 cN dtex<sup>-1</sup> in this article, which could not only inhibit the physical shrinkage, but provide chemical shrinkage for cyclization reaction.

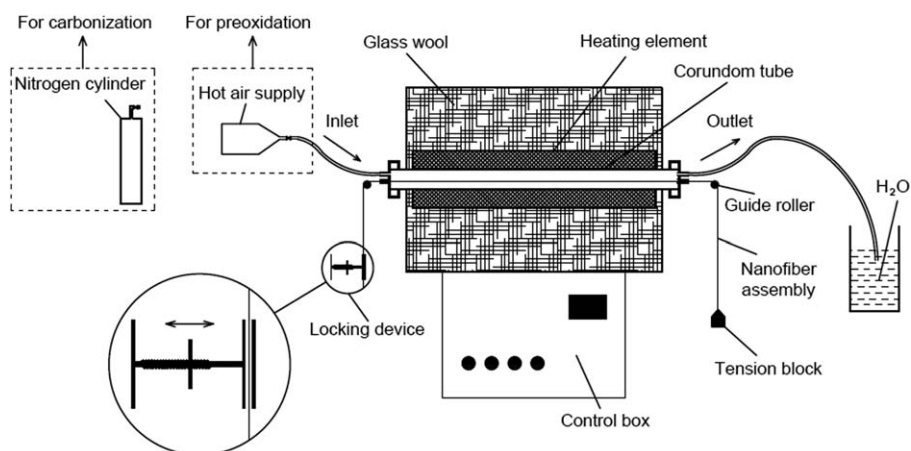
### Measurements

Preoxidation temperature (the temperature range of exothermic reaction) and cyclization degree were determined through a simultaneous thermal analyzer (STA 449 F3, NETZSCH). Heating rates were selected as 1 and 10°C min<sup>-1</sup>, respectively. Atmospheres were nitrogen and air. Cyclization degree was characterized by cyclization index (*CI*), which could be calculated through the following formula:

$$CI = \frac{H_v - H_0}{H_v} \times 100\% \quad (1)$$

In which,

*H<sub>v</sub>*—heat output of precursor fibers in nitrogen atmosphere (J g<sup>-1</sup>)



**Figure 3.** Schematic of high-temperature horizontal-type preoxidation-carbonization furnace.

$H_0$ —heat output of preoxidized fibers in nitrogen atmosphere ( $\text{J g}^{-1}$ ).

Oxygen adsorption of preoxidized fibers was obtained by an element analyzer (Vario EL III, Elementor). Group analysis for the preoxidized fibers was carried out on an infrared spectroscope (Vertex 70, Bruker) with the scanning range of  $400\text{--}4000\text{ cm}^{-1}$ , and the resolution of  $4\text{ cm}^{-1}$ . Power X-ray diffraction (X'Pert Pro, PANalytical, X-ray source was Cu radiation, analyzed range of  $2\theta$  was  $10^\circ\text{--}50^\circ$ ) was used to calculate the crystallinity ( $X_c$ ) of fibers. The corresponding formula was as follows:

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \quad (2)$$

In which,

$A_c$ —integral area of crystal peak;

$A_a$ —integral area of amorphous peak.

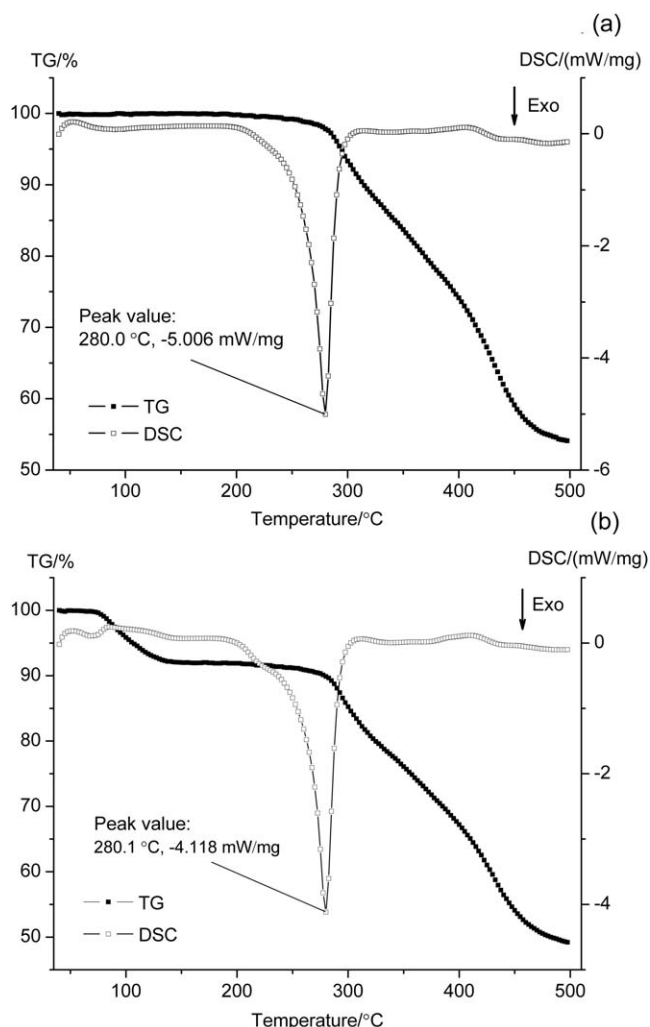
Mechanical properties were examined by Instron 5565 tensile testing machine with crosshead speed of  $10\text{ mm min}^{-1}$  and gauge length of  $10\text{ mm}$ . Appearance of the preoxidized fibers was characterized by two types of scanning electron microscopes (Vega II, Tescan; JCM-5000, JEOL). Density of fibers was measured with density gradient column, which is commonly used to test density of solid polymer. The density gradient ranges from the lowest value at the top of the column to the highest at the bottom. These limiting values are determined by two solutions prepared to fill the column. At least five floats having known densities are placed inside the column, so that the density at each position can be evaluated by a linear interpolation. Then the fiber sample after desiccation and deaeration was introduced to the column for the measurement of its density.

## RESULTS AND DISCUSSIONS

### Effect of Pretreatment on Properties of Precursor Nanofibers

**Analysis of the Content of Residual Solvent.** Figure 4 shows the DSC/TG curves of wet-spinning PAN precursor fibers and electrospun PAN nanofibers. The small endothermic peak at  $51^\circ\text{C}$  for both fibers corresponds to the volatile absorption heat of moisture in fibers. However, electrospun nanofibers has a broad gentle inclined endothermic peak between  $75$  and  $140^\circ\text{C}$  with weight loss of  $8\%$  corresponding to the volatile endothermic peak of DMF because of its high boiling point. This demonstrated that the electrospun PAN nanofibers still contained a relatively high proportion of solvents, which might cause a second dissolution of fibers during the followed drying densification process. Therefore, the residual DMF present in fibers need to be effectively removed through washing.

**Effect of Drying Densification on Fiber Density.** The evaporation of DMF during electrospinning would result in the formation of a certain number of fine holes in the electrospun nanofibers. This kind of defect should be effectively eliminated through drying densification to avoid deterioration of the properties of carbon nanofibers. Moreover, densification is beneficial to rearrangement of macromolecules in the amorphous region, which can increase macromolecules orientation to some extent.<sup>21</sup> Therefore, drying densification is a critical step to prepare carbon nanofibers from electrospun PAN nanofibers.

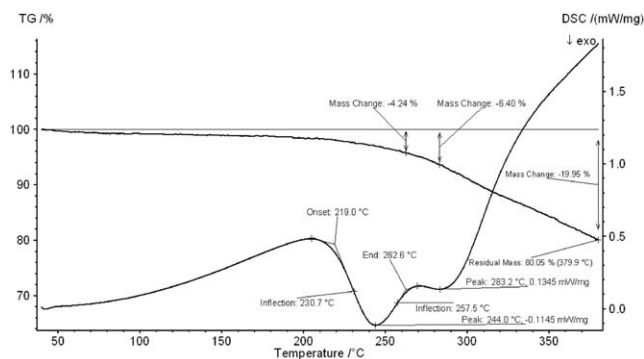


**Figure 4.** DSC/TG curves of (a) wet-spinning PAN precursor fibers and (b) electrospun PAN nanofibers in nitrogen atmosphere (Heating rate of  $10^\circ\text{C min}^{-1}$ ).

The mechanism of drying densification is to create pores in fiber collapse and close these pores with negative pressure initiated by the rapid evaporation of moisture, which is powered by external heat depending on the capillary force. Density values of wet-spinning PAN precursor fibers, electrospun nanofibers before and after drying densification were  $1.186 \pm 0.0003\text{ g cm}^{-3}$ ,  $1.159 \pm 0.0030\text{ g cm}^{-3}$ , and  $1.193 \pm 0.0036\text{ g cm}^{-3}$ , respectively. It can be seen that the density of electrospun nanofibers after drying densification was significantly increased, and even higher than the wet-spinning PAN precursor fibers, which indicates that the compact degree of nanofibers was obviously improved.

### Effect of Damp-Heat Drafting on Strength and Crystallinity of Fibers.

Prior to the fourfold damp-heat drafting, the specific breaking strength and Young's modulus of aligned electrospun nanofibers were measured to be  $0.58 \pm 0.014\text{ cN dtex}^{-1}$  and  $2.13 \pm 0.54\text{ cN dtex}^{-1}$ , which increased to  $3.02 \pm 0.35\text{ cN dtex}^{-1}$  and  $10.26 \pm 1.09\text{ cN dtex}^{-1}$  afterward, respectively. The crystallinities prior to and after fourfold damp-heat drafting were measured to be  $22.66\%$  and  $45.90\%$ , respectively. As reported in the relevant literature, crystallinity of high-



**Figure 5.** DSC/TG curve of nanofibers at the drafting ratio of 4 $\times$  in air atmosphere (Heating rate of 1 $^{\circ}\text{C min}^{-1}$ ).

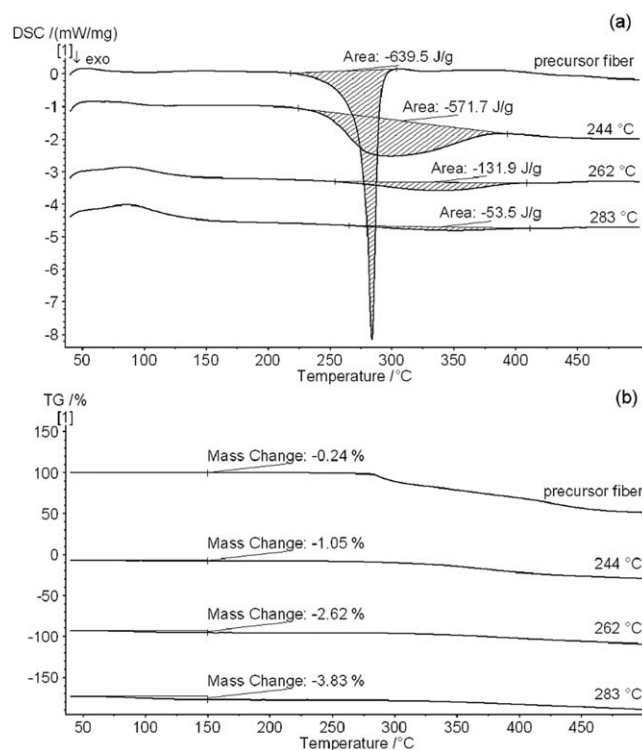
performance PAN precursor fibers should be above 45%.<sup>22</sup> Therefore, the performance of electrospun nanofibers after damp-heat drafting satisfies requirements of precursor fibers to withstand preoxidation and carbonization processes to manufacture carbon nanofibers.

### Effect of Preoxidation Temperature on Properties of Preoxidized Fibers

During preoxidation, with the gradual increase of temperature, an ideal degree of preoxidation of fibers can be achieved and side effects can be minimized due to the constant improvement of thermal stability.<sup>23</sup> In addition, two-phase carbon nanofibers, which result from the formation of skin-core structure, can be prevented. Therefore, the heating process should be kept at a relatively low rate during preoxidation. DSC/TG analysis of precursor nanofibers was carried out in air with the heating rate of 1 $^{\circ}\text{C min}^{-1}$  and results are shown in Figure 5. Two exothermic peaks appeared because of the coexistence of cyclization and oxidation. Peak temperature, onset and final temperatures of the first exothermic peak, and peak temperature of the second exothermic peak were 244.0 $^{\circ}\text{C}$ , 219.0 $^{\circ}\text{C}$ , 262.6 $^{\circ}\text{C}$ , and 283.2 $^{\circ}\text{C}$ , respectively, which could be used to determine parameters of preoxidation to ensure the sufficient cyclization and crosslinking. Therefore, three preoxidation temperatures (244 $^{\circ}\text{C}$ , 262 $^{\circ}\text{C}$ , and 283 $^{\circ}\text{C}$ ) were studied to investigate thermal properties, molecular structure, and morphology of preoxidized fibers. Holding time was set at 1 h.

**Cyclization Degree.** Figure 6 shows the DSC/TG curves of fibers preoxidized under different temperatures. Heat output of preoxidized fibers gradually decreases with the increase of heat treatment temperature, demonstrating that intrachain cyclization and interchain crosslinking occurs during preoxidation and the high-temperature-resistance ladder structure is simultaneously formed. As shown in Table I, the weight loss at 150 $^{\circ}\text{C}$  for the preoxidized fibers increases with temperature, which can be attributed to the increase of moisture content of preoxidized fibers resulting from the increase of oxygen combined on the macromolecular chain along with the dehydrogenation and oxidation reaction. *CI* for the three kinds of preoxidized fibers also increases with temperature, demonstrating that reaction degree tends to be sufficient with the increase of preoxidation temperature.

Most of the oxygen combined during preoxidation will react with hydrogen existing in PAN during the carbonization process



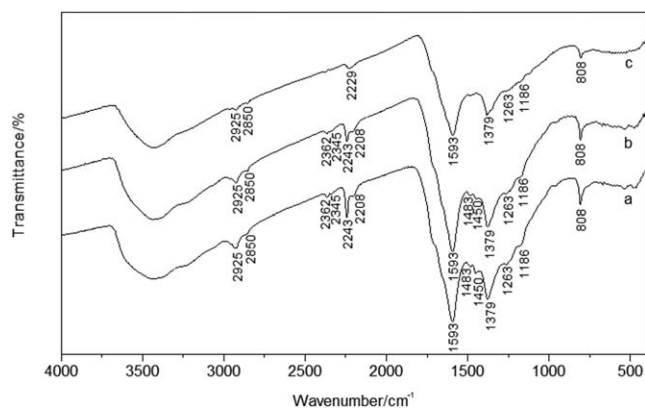
**Figure 6.** (a) DSC and (b) TG curves of nanofibers preoxidized at different temperatures (Heating rate of 10 $^{\circ}\text{C min}^{-1}$ ).

to promote crosslinking between the adjacent chains, and result in the improvement of strength and modulus of fibers. However, excess of oxygen will pull out carbon atoms from the carbon chain in the form of CO or CO<sub>2</sub> leading to the decrease of carbonization rate and deterioration of mechanical properties because of the decrease of intermolecular cohesion energy.<sup>22</sup> Through elemental analysis, oxygen adsorption of the preoxidized fibers at the preoxidation temperature of 283 $^{\circ}\text{C}$  and holding time of 1 h is 9.25%, which is in the range of reported optimum oxygen content (8–10%).<sup>24</sup>

**Molecular Structure.** Figure 7 shows the FTIR spectra of fibers preoxidized at different temperatures. The band at 2925  $\text{cm}^{-1}$  assigned to  $-\text{CH}_3$  for the stretching vibration band of C—H and the band at 2850  $\text{cm}^{-1}$  assigned to  $-\text{CH}_2-$  for the symmetric stretching vibration band of C—H appear at all the three preoxidation temperatures. At temperatures of 244 and 262 $^{\circ}\text{C}$ , two characteristic absorption bands at 2243 and 2208  $\text{cm}^{-1}$  assigning to aliphatic  $-\text{C}\equiv\text{N}$  change to one band at 2229  $\text{cm}^{-1}$  belonging to aromatic  $-\text{C}\equiv\text{N}$  when the temperature is

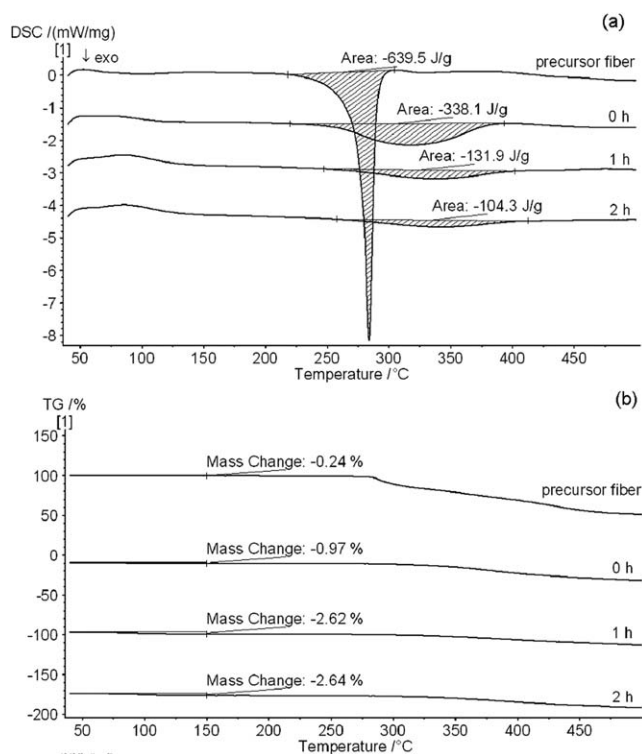
**Table I.** Weight Loss at 150 $^{\circ}\text{C}$  and Cyclization Index for Fibers Preoxidized at Different Temperatures

Preoxidation temperature ( $^{\circ}\text{C}$ )	Weight loss at 150 $^{\circ}\text{C}$ (%)	Cyclization index (%)
244	1.05	10.6
262	2.62	79.4
283	3.83	91.6



**Figure 7.** FTIR curves of fibers preoxidized at different temperatures: (a) 244°C; (b) 262°C; and (c) 283°C.

increased to 283°C. Moreover, the conjugate double peaks at 2362 and 2345  $\text{cm}^{-1}$  belonging to  $\text{CH}_2=\text{CH}-\text{C}=\text{O}$  start to disappear at this temperature. It is proved that cyclization and crosslinking reactions are carried out completely. In addition, the appearances of vibration absorption band at 1593  $\text{cm}^{-1}$  belonging to  $\text{C}=\text{O}$  on the aromatic heterocyclic ring, the characteristic stretching vibration at 1483  $\text{cm}^{-1}$  belonging to  $\text{C}=\text{N}$ , the absorption band at 1450  $\text{cm}^{-1}$  attributing to in-plane bending vibration of  $-\text{CH}_2-$ , and the stretching vibration peak at 1379  $\text{cm}^{-1}$  assigning to  $\text{C}-\text{N}$  on the aromatic heterocyclic ring further prove that the preoxidation temperature of 283°C is most suitable to ensure a complete reaction.



**Figure 8.** (a) DSC and (b) TG curves of nanofibers preoxidized at different holding times (Heating rate of  $10^\circ\text{C min}^{-1}$ ).

**Table II.** Weight Loss at 150°C and Cyclization Index for Fibers Preoxidized at Different Holding Times

Holding time (h)	Weight loss at 150°C (%)	Cyclization index (%)
0	0.97	47.1
1	2.62	79.4
2	2.64	83.6

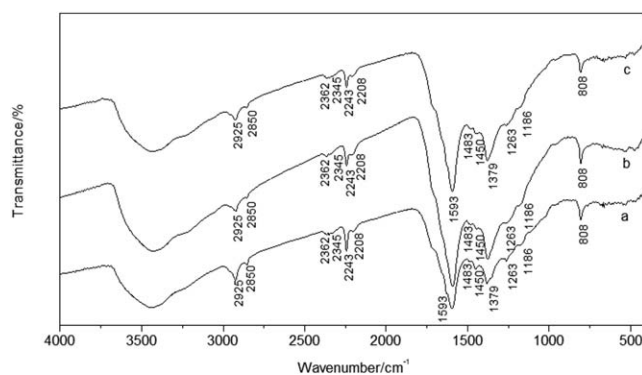
#### Effect of Holding Time on Properties of Preoxidized Fibers

Effect of holding time on properties of preoxidized fibers was studied as follows with the preoxidation temperature of 262°C.

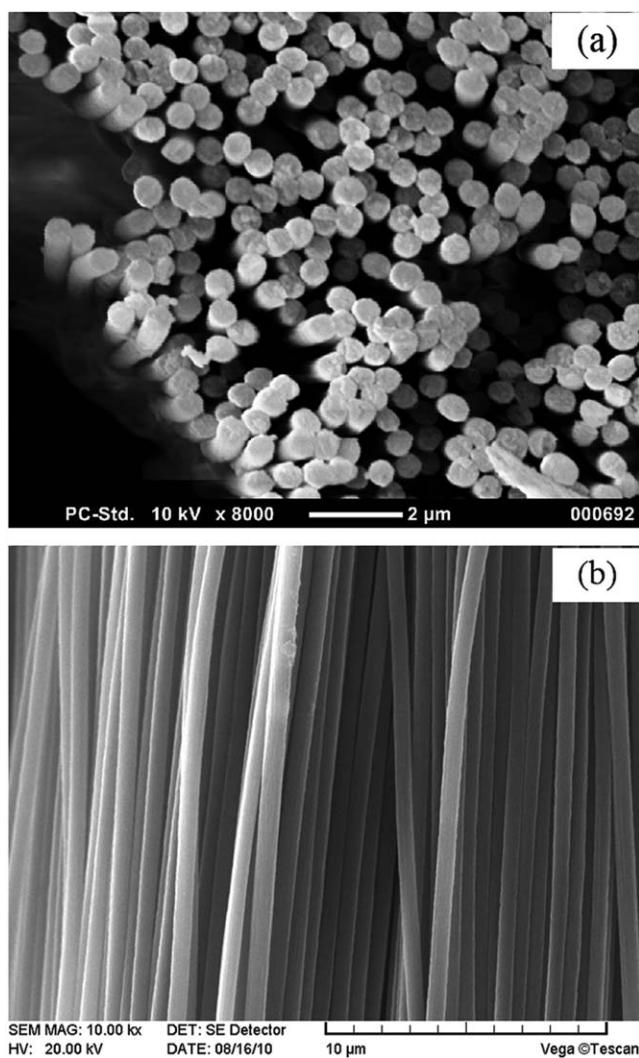
**Cyclization Degree.** DSC/TG curves of fibers preoxidized at different holding times are shown in Figure 8. Heat output of preoxidized fibers gradually decreases with the increase of holding time. As shown in Table II, *CI* of the three kinds of fibers preoxidized at different holding times is increased with holding time, while it shows a limited increase when the holding time is up to 2 h. Weight loss of preoxidized fibers at the temperature of 150°C is increased with the increase of holding time, while it also shows a minor increase when the holding time is up to 2 h. This shows that preoxidized fibers have achieved an appropriate preoxidation degree at the holding time of 1 h.

**Molecular Structure.** Figure 9 is the FTIR spectra of fibers preoxidized at different holding times. The peak location remains unchanged with the increase of holding time at the heat treatment temperature of 262°C, demonstrating that molecular bonds in the molecular chain are not changed with holding time. Therefore, in comparison to preoxidation temperature, holding time has less effect on the change of chemical structure and tends to make the reaction be more sufficient. However, preoxidation temperature is critical for fundamental change of chemical structure.

Therefore, the optimum preoxidation condition can be determined as following: preoxidation temperature of 283°C, heating rate of  $1^\circ\text{C min}^{-1}$ , and holding time of 1 h. The obtained preoxidized fibers possess a sufficient cyclization and crosslinking. The second peak in the DSC curve shown in Figure 5 is due to dehydrocyclization reaction, and not the excessive preoxidation. Cross-section and longitudinal appearance of the corresponding preoxidized fibers are given in Figure 10. Uniformity of fibers and the circular cross-section can ensure an even force during



**Figure 9.** FTIR curves of nanofibers preoxidized at different holding times: (a) 0 h; (b) 1 h; and (c) 2 h.



**Figure 10.** (a) Cross-section and (b) longitudinal appearance of the fibrous bundle preoxidized at 283°C (Heating rate of 1°C min<sup>-1</sup> and holding time of 1 h).

drafting in the process of preoxidation and carbonization. Moreover, the smooth fiber surface indicates that adhesion does not occur between fibers. Therefore, optimum properties of carbon nanofibers are expected to be obtained when preoxidized fibers are prepared as above for precursors.

## CONCLUSION

Washing, drying densification, and damp-heat drafting on electrospun PAN nanofibers can remove the residual solvent, improve compactness, and crystallinity to prepare precursors for manufacturing high quality carbon nanofibers. Meanwhile, the pretreated nanofibers should be applied a tension during preoxidation to prevent the disorientation of molecules and control shrinkage of fibers during high temperature treatment. Fibers in the fibrous bundle prepared in this article show a high alignment degree along the longitudinal direction, which can ensure the tension be fully acted on every nanofiber to achieve a preferred orientation. Therefore, carbon nanofibers with good properties are expected to be obtained after further carbonization.

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