

# Effects of Preoxidation and Carbonization Technologies on Tensile Strength of PAN-Based Carbon Fiber

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**ABSTRACT:** Dependence of the tensile strength of resulting carbon fiber (CF) on the preparation technologies during preoxidation and carbonization were studied systematically by a series of pilot experiments. The proper preoxidation time, preoxidation temperature, and preoxidation stretching ratio are the base of preparing high-quality CF. During precarbonization, the enhancement of the precarbonization temperature and the application of the precarbonization stretching are helpful to increase the tensile strength of CF, but the stretching ratio should be

controlled carefully by on-line tension values. The tensile strength of CF increases quickly below 1200°C and then slowly above 1200°C as the carbonization temperature raises. Even though during carbonization, a proper relaxation should also be explored in order to prepare optimal CF. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1259–1264, 2008

**Key words:** stabilization; precarbonization; carbonization; processing; strength; preoxidation

## INTRODUCTION

Carbon fiber (CF) has been given much attention since it was born in the fifties of the twentieth century. The modern preparation of high-strength CF from polyacrylonitrile (PAN) precursor fiber is carried out on a serial production line, including a preoxidation in air followed by a precarbonization and a carbonization in an inert atmosphere.<sup>1,2</sup> Preoxidation is to pass the precursor tow through a furnace divided into several zones with increasing temperature gradient at 200–300°C in air, during which PAN macromolecules are converted into heat-resistant ladder polymer structure.<sup>3</sup> Successively, a precarbonization treatment at 300–700°C is performed prior to carbonization in order to avoid the thermal shock of the fiber when carbonized.<sup>1</sup> A highest temperature of 1400–1600°C and a total residence time of only a few minutes in oxygen-free atmosphere are applied during carbonization to drive off the noncarbon elements and produce the high-strength inorganic carbonaceous fibrous materials

at last. Although the tensile strength of CFs is, to a great extent, determined by the quality of the precursor and the precursor fibers whereas preoxidation and carbonization merely refine and perfect the as-spun structure,<sup>4</sup> it is not to say the latter is unimportant. Because for given PAN precursor fiber none but the rational and proper preoxidation and carbonization technologies can shape the optimal structure of the fiber and accomplish the anticipative property. Thus, much attention has been paid to optimize the processing conditions during preoxidation and carbonization, and some correlative studies are also available.<sup>5–20</sup> However, most of the previous studies<sup>9,10,13–20</sup> were only limited to the effect of one single parameter on the properties of CF and did not consider the multiple parameters of continuous production systematically. In addition, some research<sup>6,7,10</sup> was done by using the laboratory experiments which are different from the industrial manufacture. In this article, the effects of seven essential parameters on the tensile strength of CF were explored by a series of experiments in a pilot line, which is expected to provide some valuable information for the CF fabrication.

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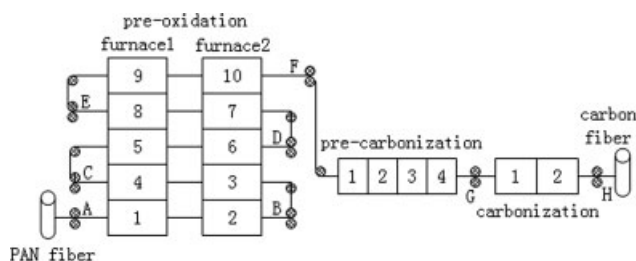
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## EXPERIMENTAL

### Materials

A free-radical copolymerization of 99.4 wt % acrylonitrile and 0.6 wt % ammonium itaconate [IA(NH<sub>4</sub>)<sub>2</sub>]

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**Figure 1** The processing flow of preoxidation and carbonization.

was initiated by azodiisobutyronitrile (AIBN) in dimethylsulfoxide (DMSO) solution. The dope, which consists of 23% copolymer with an average molecular weight of  $1.4 \times 10^5$ , was then spun with a wet spinning technique to the precursor fibers containing 1000 filaments each single tow. The titer, the tensile strength, and the elongation of single filament were 1.1 dtex, 800 MPa, and 10 %, respectively.

### Preoxidation and carbonization experiments

Figure 1 shows the preparation process of CF. The precursor fibers pass continuously through two oxidizing furnaces with 10 temperature zones, one pre-carbonization furnace with four zones and one carbonization furnace with two zones. Eight pairs of driving wheels are set in the positions of A–H, respectively, in order to control the running speed of the fibers, the time of preoxidation and carbonization, and different drawing ratio between every two driving wheels.

Seven processing parameters, which determine three kinds of fiber structures, are divided into three categories as seen in Figure 2. A series of experiments were carried out by changing one of the seven parameters while setting the other six as the reference values listed in Table I.

1. Experiments on preoxidation time: Four kinds of running speeds 0.2, 0.3, 0.4, and 0.5 m/min were selected as the initial feeding speeds. Four oxidized PAN fibers experiencing different pre-oxidation time of 120, 80, 60, and 48 min could be obtained.
2. Experiments on preoxidation temperature: The temperatures of 1–9 zones were the same as the corresponding reference values in Table I. But various temperatures of 210, 230, 240, 250, 260, and 275°C were set in the rearmost zone, respectively. Six oxidized fibers were prepared.
3. Experiments on preoxidation stretching ratio: Three different drawing ratio values, 6.00%, 8.00%, and 9.00%, were applied between drawing wheels A and C of preoxidation furnace in

Figure 1 to produce three different CFs. Between drawing wheels C and F, the stretching ratios were all zero.

4. Experiments on precarbonization temperature: The temperatures of 1–3 zone in precarbonization furnace were set as 300, 350, and 500°C but the temperature of the 4th zone differed from 500 to 750°C, at 50°C intervals.
5. Experiments on precarbonization stretching ratio: Seven plus- or minus- stretching ratio were used between F and G in Figure 1 during pre-carbonization, viz. –1.5%, –1.0%, 0.5%, 2.51%, 2.71%, 2.85%, and 3.00%.
6. Experiments on carbonization temperature: Three different temperature settings of 1000–1000°C, 1200–1200°C, and 1280–1400°C were chosen to carbonize the fiber.
7. Experiments on carbonization stretching ratio: Three minus-stretching ratios of –3.50%, –4.24%, and –5.00% were employed between G and H in Figure 1 during carbonization.

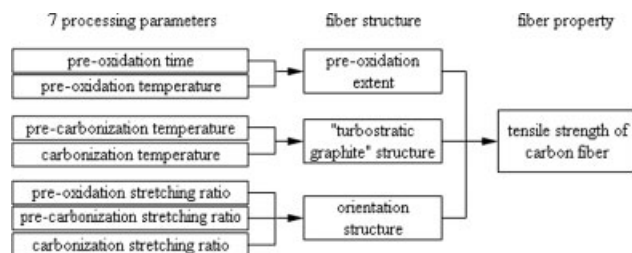
### Characterization

The density of oxidized PAN fiber was obtained at 25°C by a sink/float method in a mixture of *n*-heptane and carbon tetrachloride. The mass percentage content of oxygen (O) element was obtained by elemental analysis measurement in German GmbH Vario EL III elemental analyzer. German DXF-400 Tension Tester was used to measure the tension in fibers between two adjacent driving wheels on line. The tensile strength of CF multifilament was tested by RGD tensile-testing machine (made in Shenzhen, China) at a crosshead speed of 10 mm/min with a test-gauge of 200 mm for all samples.

## RESULTS AND DISCUSSION

### The effect of the preoxidation temperature and time on the strength of CF

Figures 3 and 4 illustrate that the oxygen contents and densities of oxidized fibers are a function of dif-



**Figure 2** Relation of processing parameters, fiber structures, and fiber property.

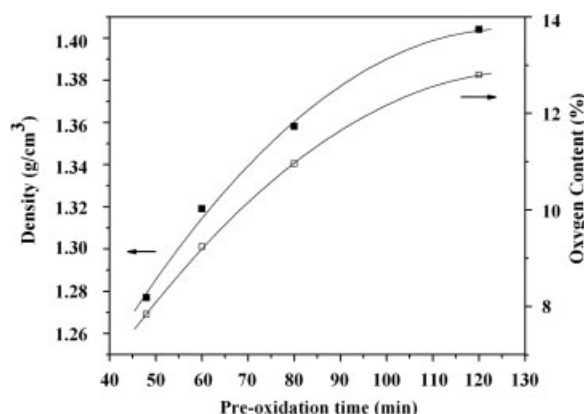
**TABLE I**  
The Reference Values of Seven Essential Processing Parameters

Parameters	Preoxidation	Precarbonization	Carbonization
Temperature of zones (°C)	10 zones: 195–205–225–235–245–255–265–275–275–255	4 zones: 300–350–500–600	2 zones: 1280–1400
Step stretching ratio (%)	Between drawing wheels A and C: 5.00 Between drawing wheels C and F: 0.00	Between drawing wheels F and G: 1.50	Between drawing wheels G and H: –4.00
Running speed (m/min)	0.40 (initial feeding speed, it will change a little after applying stretching ratio)		

ferent time or different temperature. The oxygen content and density of the oxidized fiber increase gradually with elongating preoxidation time or raising temperature in rearmost zone due to the occurrence of the cyclization, aromatization, and oxidation reactions. The more the oxygen content and the density of the fiber are, the more stable the fiber structure is. However, the tensile strength of resulting CF is not direct proportion to the structure stability of oxidized PAN fiber. Our previous studies<sup>21</sup> indicated that those oxidized PAN fibers whose oxygen content lies near or between 10 and 12% may produce good CFs; otherwise, it does not. Excessive or insufficient preoxidation is bad for the preparation of CF.<sup>2</sup> Thus, the appropriate preoxidation time and temperature are necessary, because they can control the oxygen content and density of the oxidized PAN fiber within optimum range and also guarantee the heat-resistance quality of the fiber structure. Moreover, the combination of the short preoxidation time and the high temperature in the rearmost zone can also promote the efficiency and cut the cost.

#### The effect of the preoxidation stretching on the strength of CF

The experimental results obtained by using different preoxidation stretching ratios are tabulated in Table II.

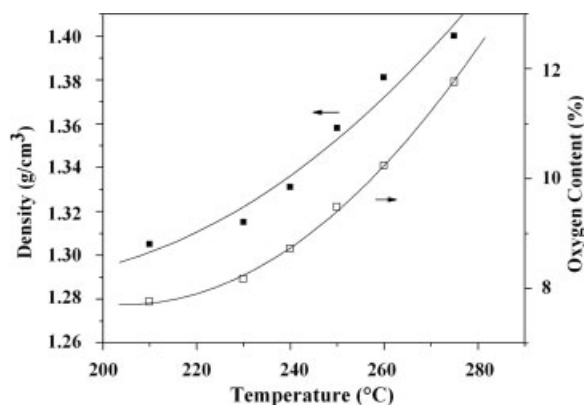


**Figure 3** Oxygen content and density of oxidized fibers as a function of different temperature in the rearmost pre-oxidation zone.

The on-line tension and tensile strength of resulting CF increase with the enhancement of the preoxidation stretching ratios. The stretching restrains the physical shrinkage of the molecular chains at the initial stage of preoxidation and forms the orientation of the PAN macromolecules and subsequently of the ladder structure.<sup>2</sup> At the same time, the limit to the shrinkage of the fiber brings the internal stress, which can be measured by the tension tester. The larger the stretching ratio applied is, the better the orientation of the fiber is, and the more the internal stress is. This orientation and internal stress are kept in the structure of the fiber till the formation of the CF. Thus, the on-line tension during precarbonization and carbonization is strongly affected by the preoxidation stretching extent, and the same is true with the strength of resulting CF as shown in Table II.

#### The effect of the precarbonization and carbonization temperature on the strength of CF

Figure 5 exhibits the relation between the tensile strength of CFs and the temperatures of precarbonization. The tensile strength of CFs at first increases gradually till 650°C, then declines a little at 700°C and comes to the top at 750°C. This result is different from the previous study,<sup>9</sup> in which the strongest tensile strength of CF occurred when the precarbonization temperature reached 550°. How the precarbo-



**Figure 4** Oxygen content and density of oxidized fibers as a function of different preoxidation time.

**TABLE II**  
On-Line Tension and Strength of Fiber Prepared by Different Preoxidation Stretching Ratio

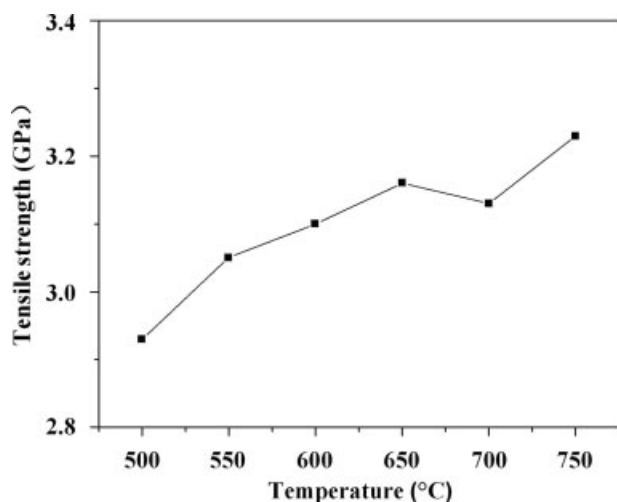
Stretching ratio between A and C (%)	On-line tension in precarbonized fiber (cN)	On-line tension in carbonized fiber (cN)	Tensile strength of carbon fiber (GPa)
6.00	110	257	2.49
8.00	120	282	2.66
9.00	125	290	2.75

nization temperature affects the tensile strength of CF is still not clear at all. Maybe, it is related to the chemical reactions during precarbonization and the elementary formation of the carbon basal planes.<sup>22–24</sup> After all, adjusting the precarbonization temperature can improve the tensile strength of CF.

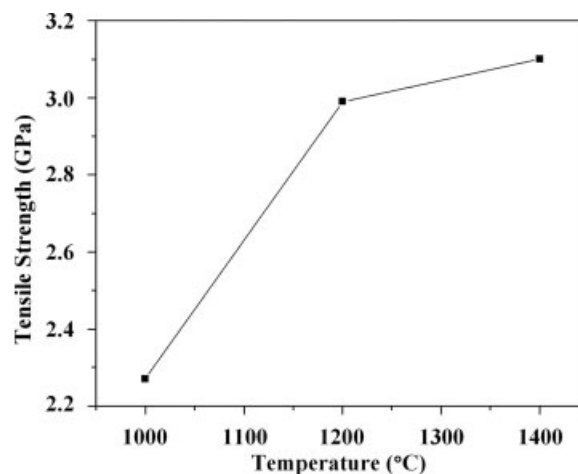
Figure 6 presents the tensile strengths of CF at the carbonization temperature of 1000, 1200, and 1400°C. As the temperature raises, the tensile strength of CF increases quickly below 1200°C, and then slowly above 1200°C. It can be explained by the development of the quantity and the size of the turbostratic graphite-like plane stacks along the axial direction of the fiber below 1600°C.<sup>9,10,25</sup> Below 1200°C, a mass of the turbostratic graphite-like plane stacks form due to the elimination of most nitrogen element in fiber, resulting in the quick increase of the tensile strength with the enhancement of the carbonization temperature.<sup>24,26</sup> But above 1200°C, the structure of CF is merely further perfected and refined, which brings the slow improvement of the tensile strength of CF.

#### The effect of the precarbonization and carbonization stretching on the strength of CF

Tables III and IV list the tensile strengths of CF prepared by applying different relaxation extent



**Figure 5** Tensile strength of carbon fiber as a function of precarbonization temperature.



**Figure 6** Tensile strength of carbon fiber as a function of carbonization temperature.

(minus-stretching ratio) or stretching extent (plus-stretching ratio) during the precarbonization of 300–600°C. The results in Table III indicate that the application of stretching during precarbonization is good for the preparation of CF. When experiencing precarbonization treatment, the oxidized PAN fiber can shrink due to the cross-linking reactions and the pyrolysis of the remaining linear molecules. The shrinkage can destroy the orientation established by the preoxidation stretching.<sup>2,27</sup> Thus, the resistance to the shrinkage of the fiber during precarbonization can keep the orientation of the fiber and accordingly enhance the tensile strength of the CF. Further experiments also demonstrate that the tensile strength of CF increases with the increase of the stretching ratio during precarbonization, as listed in Table IV. Moreover, to our particular surprise, the strength is so sensitive to the tiny change of the stretching ratio value during precarbonization.

However, too much plus-stretching ratio should be avoided because the structure of the oxidized fiber is rigid ladder polymer but not flexible linear macromolecular. The on-line tension values in fiber, which may help to judge whether the stretching ratio applied currently is suitable, deserve more attention. For a tow PAN fiber of 1000 filaments with 1.1

**TABLE III**  
On-Line Tension and Strength of Fiber Prepared by Applying Plus- and Minus- Stretching Ratio During Precarbonization

Precarbonization stretching ratio (%)	On-line tension in precarbonized fiber (cN)	On-line tension in carbonized fiber (cN)	Tensile strength of carbon fiber (GPa)
–1.5	106	240	2.42
–1.0	108	249	2.49
+0.5	150	270	3.11

**TABLE IV**  
On-Line Tension and Strength of Fiber Prepared by Different Precarbonization Plus-Stretching Ratio

Precarbonization stretching ratio (%)	On-line tension in precarbonized fiber (cN)	On-line tension in carbonized fiber (cN)	Tensile strength of carbon fiber (GPa)
2.51	138	250	3.50
2.71	148	250	3.63
2.85	150	252	3.71
3.00	158	270	3.75

dtex in titer, stretching ratio applied should make the online tension value remaining at 150 cN or so during precarbonization and within 200–300 cN during carbonization.

When precarbonized fiber continues to be carbonized at 1400–1600°C; certain relaxation is essential due to a considerable shrinkage generated by the structural rearrangement, otherwise the filament would rupture. However, redundant and deficient relaxation extent can both reduce the strength of CF as shown in Table V. On earth, how much minus-stretching ratio is optimal during carbonization needs to be explored according to the preoxidation and precarbonization processing conditions.

### Optimal preoxidation and carbonization technologies

In fact, the optimal processing parameters of the CF manufacture depend on the PAN precursor fiber itself, including its copolymer composition, physical property, thermal properties, and so on. For the PAN fiber described in the experimental section, the optimum values of seven parameters are given in Table VI, by using which we can prepare the best CF.

## CONCLUSIONS

High-strength PAN fiber does not always produce high-strength CF because processing conditions of preoxidation and carbonization also play an important role during the conversion from PAN fiber to CF. For given PAN fiber, the tensile strength of

**TABLE V**  
On-Line Tension and Strength of Fiber Prepared by Different Carbonization Minus-Stretching Ratio

Carbonization stretching ratio (%)	On-line tension in carbonized fiber (cN)	Tensile strength of carbon fiber (GPa)
–3.50	310	2.42
–4.24	200	3.48
–5.00	161	3.30

**TABLE VI**  
The Optimal Values of Seven Processing Parameters for PAN Fibers Prepared by Ourselves

Parameters	Preoxidation	Precarbonization	Carbonization
Temperature of zones (°C)	195–205–225–235–245–255–260–275–275–255	273–350–500–750	1280–1400
Step stretching ratio (%)	(AC-CF): 6.00–0.00	(FG): 2.00	(GH): –4.00
Running speed (m/min)	0.4 (initial feeding speed, it will change a little after applying stretching ratio)		

resulting CF is greatly influenced by seven parameters as follows:

1. Proper preoxidation time and temperature can assure the appropriate oxygen content and structure stability of oxidized fiber. The stretching at the initial stage of the preoxidation process causes the orientation of the PAN macromolecules and subsequently of the ladder structure. Both above lay the groundwork for the preparation of high-strength CF.
2. Within the experimental temperature range, the tensile strength of CF increases with raising precarbonization temperature and reaches the maximum at 750°C. The application of precarbonization stretching is helpful to keep this orientation which has been established in the preoxidation process. It is noticeable that the stretching ratio must be controlled gingerly by on-line tension values, otherwise the filaments would break.
3. As the temperature raises, the tensile strength of CF increases quickly below 1200°C and then slowly above 1200°C. Even though during carbonization, a proper relaxation should also be explored in order to prepare optimal CF.

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