

# Influence of Tension on the Oxidative Stabilization Process of Polyacrylonitrile Fibers

Gangping Wu,<sup>1</sup> Chunxiang Lu,<sup>1</sup> Licheng Ling,<sup>2</sup> Aimin Hao,<sup>1</sup> Fu He<sup>1</sup>

<sup>1</sup>Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China

<sup>2</sup>College of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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**ABSTRACT:** Polyacrylonitrile fibers were heat-treated in air, and a series of stretching experiments were conducted in different temperature zones. The effects of tension on the microstructure of the heat-treated fibers and the tensile strength of the resultant carbon fibers were investigated. The results show the variations in morphological characteristics affected by stretching were different as stabilization proceeded. A possible mechanism of tension on cyclization and, thus, stabilization was elucidated. During stabilization, ten-

sion at low temperatures led to a great increase in the tensile strength of the carbon fibers, whereas tension at high temperatures resulted in only small improvement in the tensile strength of the carbon fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1029–1034, 2005

**Key words:** differential scanning calorimetry (DSC); stabilization; tension

## INTRODUCTION

Polyacrylonitrile (PAN) fiber is one of the most suitable precursors for carbon fibers. Among the manufacture of carbon fibers, the oxidative stabilization of a precursor fiber is an essential step in making the precursor infusible at high-temperature carbonization;<sup>1–3</sup> the process is also considered the most important because it largely governs the final structure and mechanical properties of the carbon fiber.<sup>4</sup>

The application of tension during stabilization is established<sup>1,5,6</sup> to prevent polymer chains from relaxing and losing their orientation, which becomes locked in through crosslinking. The preferred structures lead to carbon fibers with high orientation and, thus, superior tensile properties. Numerous studies<sup>7,8</sup> have shown that the mechanical properties of carbon fibers improve with increasing tension during stabilization. Bahl and Mathur<sup>9</sup> found that there existed an optimum load during stabilization, and any underload or overload deteriorated the final tensile strength. So, the rearrangement of hot stretching during stabilization has been deemed as a routine for the production of

high-strength and high-modulus PAN-based carbon fibers. Wang<sup>10</sup> reported that prestretching had a significant influence on the physical shrinkage of PAN fibers and attributed it to the variation of morphological order. The top-grade carbon fibers (T-1000), which were manufactured by Toray Industry, Inc., had a tensile strength of 7.06 GPa and a Young's modulus of 490 GPa, although the production details were kept secret. However, the smaller diameters and fewer defect of the fibers have been confirmed. Although many studies have been carried out to determine the proper stabilizing conditions, including tension, to improve the quality of final carbon fibers, some problems still remain regarding how the process variation during stabilization affects the structure and performance of the carbon fiber.

Recently, Gupta and Harrison<sup>11</sup> indicated that stabilization reactions occur preferably in one of the phases, first in the amorphous domain and then in the crystalline region. This has been confirmed in our laboratories. We found that crystalline morphology was largely reserved at the initial stage, with a considerable number of nitrile groups markedly vanishing. In addition, analysis from the orientation of the crystalline region also showed an initial rigid structure and subsequent relaxed structures during stabilization. These results attempt to show that inducing varying orientations and orders in the fiber at different stabilization stages might have a distinct influence on the thermorheological response, even the thermal reaction behavior of the fibers. In this study, various

Correspondence to: C. Lu or G. Wu (lucx@sxicc.ac.cn).

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TABLE I  
Properties of the PAN Fibers

Filaments in a bundle	Tensile strength (GPa)	Elastic modulus (GPa)	Elongation (%)	Diameter ( $\mu\text{m}$ )	Shrinkage in boiling water (%)
3000	0.47	5.67	15.99	12.06	5.1

tensions were applied in different stages to alter the orientation and order of the precursor fibers. The effect of tension on the stabilization process and the properties of the carbon fibers are discussed.

## EXPERIMENTAL

### Precursor fibers and stabilization

The precursor fibers were prepared in our laboratories and contained 1% itaconic acid. Their properties are shown in Table I. Stretching treatment of the fibers was carried out on a stabilization furnace as previously reported<sup>12</sup>. The fibers were heat-treated from ambient temperature up to the investigated temperatures at 1°C/min, with a constant tension of 2 N (0.2 kgf). Then, a study of the influence of various tensions was carried out in the following temperature range (160–190, 190–210 and 210–230 °C).

### Wide-angle X-ray diffraction (WAXD) analysis

A Rigaku X-ray powder diffractometer (Rigaku Company, Tokyo, Japan) with Cu  $K_{\alpha}$  radiation as a source was used to study the wide-angle diffraction pattern. The step interval was 0.02°. The average size of the laterally order domains ( $L_c$ ) also referred to as crystal size, was estimated with the Scherrer equation:

$$L_c = K\lambda/B_0 \cos\theta \quad (1)$$

where  $\lambda$  is the wavelength of the X-rays;  $B_0$  is the full width at half the maximum intensity (FWHM), which was estimated from the (100) peak at  $2\theta = 17^\circ$ ; and  $K$  is a constant value, assigned as 0.89. The inhomogeneous strains were not corrected, so the estimations obtained here were more or less lower than the actual crystal sizes.

The aromatization index (AI) was determined by the following equation:

$$\text{AI} = I_a/(I_a + I_p) \quad (2)$$

where  $I_a$  is the intensity of diffraction at  $2\theta = 25^\circ$ , which is given by the ladder structures, and  $I_p$  is the diffraction intensity of the PAN crystal at  $2\theta = 17^\circ$ .

We measured the orientation in crystalline ( $\pi$ ) by the X-ray diffraction technique, scanning the fibers

around  $2\theta = 17^\circ$ , and then the degree of orientation was determined by the following equation:

$$\pi(\%) = (180 - H)/180 \quad (3)$$

where  $H$  is the FWHM at  $2\theta = 17^\circ$  diffraction.

### Thermal analysis

Differential scanning calorimetry (DSC) was carried out in a Netzsch 409PC machine (Netzsch, Germany) under nitrogen. The scanning range was 25–450°C, and the heating rate was 10°C/min.

### Mechanical properties

The mechanical properties of the carbon fibers were measured with a tensile-testing machine (Taicang Textile Machinery Co., LTD., China) at a crosshead speed of 1 mm/min with a testing length of 20 mm and a load cell of 20 g. In each case, at least 30 samples were tested, and the average value was obtained. The diameter of each fiber was measured on an Olympus microscope before the tensile test.

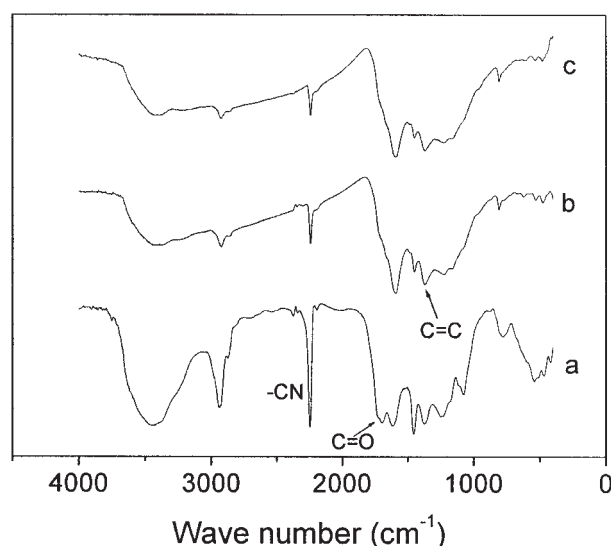


Figure 1 Fourier transform infrared spectra of the fibers with different heat treatment temperatures (HTTs): (a) 190, (b) 210, and 230°C.

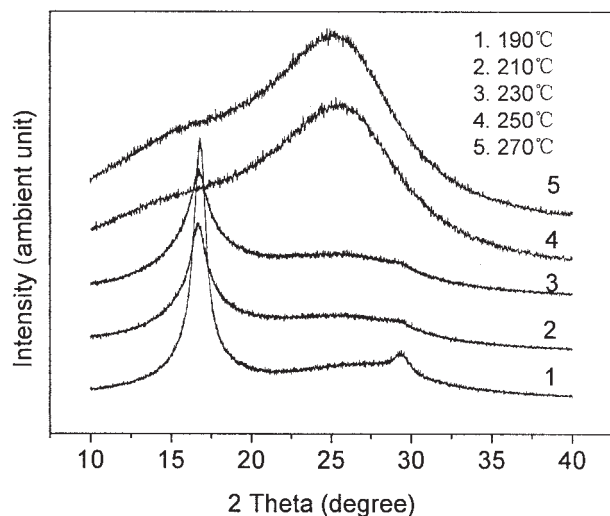


Figure 2 WAXD profiles of the fibers with different HTTs.

## RESULTS AND DISCUSSION

### Stabilization

The IR studies (shown in Fig. 1) indicated a prominent adsorption peak at  $1688\text{ cm}^{-1}$ , which was attributed to the stretching vibration of carboxyl groups in the comonomers. The adsorption was significant at  $190^\circ\text{C}$  and vanished up to  $210^\circ\text{C}$ , with a simultaneous tendency toward a large decrease in the adsorption intensity at  $2240\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  groups) and  $2930\text{ cm}^{-1}$  ( $\text{C}-\text{H}$  groups). This was direct evidence of the onset of stabilization reactions. Warner et al.<sup>13</sup> proposed there exist two major phases in the fibers, a laterally ordered phase and a less ordered one. In addition, previous studies<sup>11</sup> with small-angle X-ray scattering have shown that stabilization reactions occur preferably in one of the phases. The stabilization reactions are

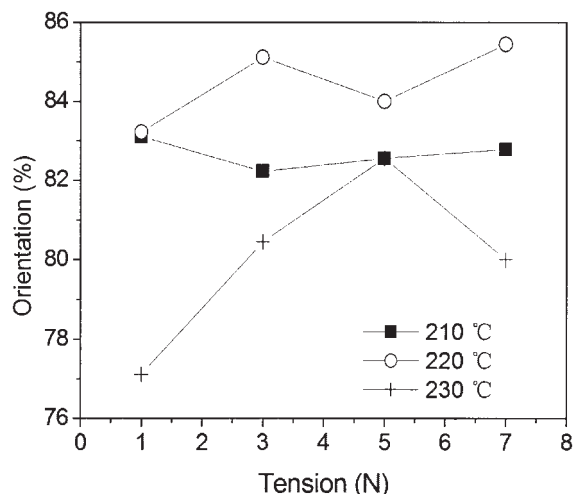


Figure 3 Changes in the orientation of fibers heated to different HTTs with increasing tension.

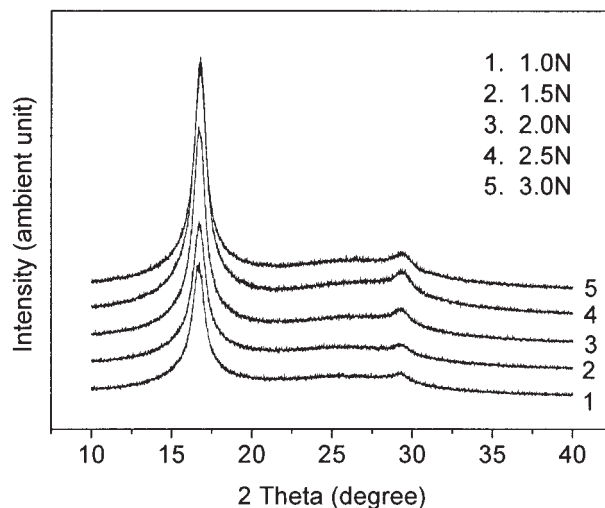


Figure 4 Change in the WAXD pattern of the fibers with increasing tension before stabilization.

most likely take place in the amorphous region because comonomers are present in the amorphous region, and oxygen diffuses easily into an amorphous phase of low density as compared to a rigid crystalline region. It is also expected that morphological structures are largely reserved up to  $230^\circ\text{C}$  (as shown in Fig. 2), and orientation in the crystalline region before  $230^\circ\text{C}$  (as shown in Fig. 3) remains basically unchanged with its rigid structure. At  $230^\circ\text{C}$ , the orientation in the molecular chains were quite easily affected by increasing tension compared to that below  $230^\circ\text{C}$  (shown in Fig. 3), suggesting that the stabilization reactions started to propagate into the crystalline zone. These results led us to divide the stabilization process roughly into three temperature zones:  $160-190$ ,  $190-210$ , and  $210-230^\circ\text{C}$ , corresponding to the zone before stabilization, major stabilization in the amorphous region, and stabilization in the crystalline regime, respectively. The division is rather rough, but it does not influence our discussion.

### Effect of tension on the progression of stabilization

The WAXD patterns are shown in Figure 4. Generally, the spectra of PAN fibers showed a sharp intense

TABLE II  
Effect of Tension on the Crystalline Structures Between 160 and  $190^\circ\text{C}$

Sample No.	Tension (N)	$d$ (100) (Å)	$L_c$ (100) (nm)
1	1.0	5.3296	14.52
2	1.5	5.2979	13.94
3	2.0	5.3011	14.52
4	2.5	5.2760	22.75
5	3.0	5.2729	23.55

**TABLE III**  
Effect of Tension on the Crystalline Structures Between 190 and 210°C

Sample No.	Tension (N)	$d$ (100) (Å)	$L_c$ (100) (nm)	AI (%)
1	1.0	5.3106	75.00	19.19
2	1.5	5.3042	21.14	29.46
3	2.0	5.3042	51.96	32.70
4	2.5	5.3169	37.51	29.73
5	3.0	5.2419	30.69	40.70

diffraction at  $2\theta = 16\text{--}17^\circ$  and a weak intense diffraction at  $2\theta = 29.5^\circ$ , with a broad scattering maximum situated around  $2\theta = 25\text{--}27^\circ$ . The sharp and intense diffraction corresponded to a lateral repeat distance that was represented as a (100) diffraction in hexagonal lattice. The reflection at  $2\theta = 29^\circ$  confirmed a second-order structure of (100) diffraction. As shown in Figure 4, for those samples of prestretching before stabilization (up to 160–190°C), the (100) diffractions were greatly intensified and sharpened with increasing tension. The structural parameters of these fibers evaluated from the WAXD pattern are shown in Table II. The  $d$ -spacings of (100) diffraction decreased, and the apparent crystallite size increased with increasing tension. These variations were due to the increased perfection at the crystallite boundaries and enhanced the degree of crystallinity. Raskovic and Marinkovic<sup>14</sup> reported that PAN homopolymer fibers showed a significant endotherm at this temperatures (160–180°C) by differential thermal analysis and related it to molecular rearrangements. So, one can conclude that stretching offers molecular chains additional energy to readjust and pack into an ordered phase in the amorphous region.

For the treated fibers up to 190–210°C, the structural parameters evaluated from WAXD analysis are shown in Table III, which shows a decreased trend in crystallite size for the (100) diffraction with increasing tension, implying that stabilization reactions occurred around the crystallite boundaries, perhaps among the rearranged order portion. The amount of stabilized reactions evidenced by AI values increased with increasing tension, indicating that stretching promoted the reactions. Results from DSC measurement in ni-

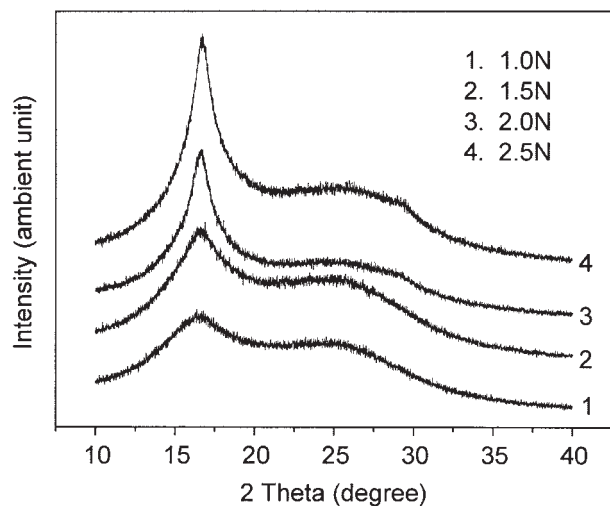
trogen for the treated fibers are given in Table IV. According to the data, (1) the threshold and peak temperatures showed a decreasing trend with increasing in tension, and (2) the total heat, however, generally decreased. For fibers stabilized in nitrogen, only a cyclization reaction occurred. Thus, the decrease in threshold and peak temperatures suggested that the stretching on PAN fibers facilitated the cyclizations. Exothermic heat was produced by the cyclization reactions of pendant nitrile groups of PAN fibers treated in nitrogen. Thus, more released heat suggested that more nitrile groups were taking part in the cyclization. In fact, stretching affected the readjustment of the molecular chains (involving the rotation of nitrile groups around the C—C single bond) not only in the ordered domains but also and especially in the disordered domains. This might have brought more nitrile groups into a suitable position for cyclization and, therefore, led to a higher heat flow. This variation of heat flow can be concluded from the apparent decreasing exotherm, because it was measured after treatment. Raskovic and Mannkovic<sup>14</sup> observed that low temperatures result in molecular rearrangement in the fibers, but the effect on cyclization is detected only when the sample treated for more than 5 h at 220°C. This may have been due to the difference in precursor fibers.

For the samples heat-treated up to 210–230°C, a strong dependence of the WAXD pattern on the stretching was evident (shown in Fig. 5 and Table V). That is, with increasing stretching, the (100) diffraction tends to be lower and broader. In addition, the AI values, which is a representation of stabilization reactions, shifted to a lower value. These results indicate the stretching has a depressing effect on cyclization.

The initiation of cyclization depends on steric factors of the PAN molecule. It is very important to bring the adjacent nitrile groups into the right position for the initiation of cyclization.<sup>15</sup> The steric structures are the function of molecular mobility, heat, and tension, which is responsible for the rotation and rearrangement of nitrile groups. Very probably at low temperatures (i.e., 160–190°C), the ordered phase contained a great number of intermolecularly bound nitrile groups, which left fewer free nitrile groups. In contrast, the molecular chains in the amorphous phase

**TABLE IV**  
Effect of Tension on the DSC Pattern Between 190 and 210°C

Sample No.	Tension (N)	Starting temperature (°C)	Peak temperature (°C)	Ending temperature (°C)	Exotherm (J/g)
1	1.0	245.2	277.6	311.5	398.0
2	3.0	242.9	277.7	314.3	371.1
3	5.0	245.5	272.7	318.4	374.8
4	7.0	242.0	271.3	317.6	364.9

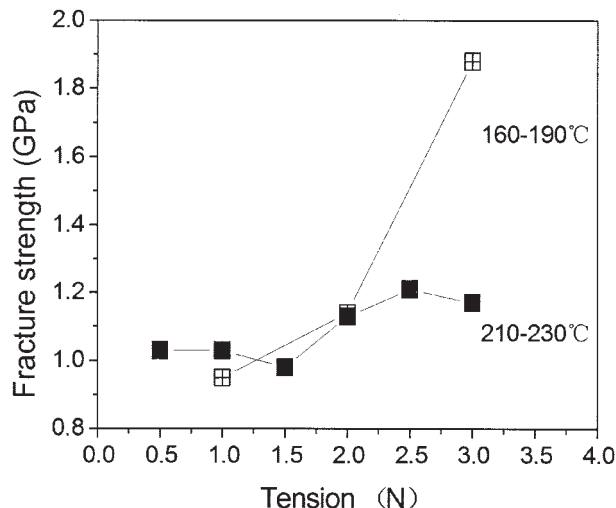


**Figure 5** Effect of tension on the WAXD patterns during stabilization between 210 and 230°C.

were flexible.<sup>16</sup> Thus the stretching and segmental mobility led the molecular chains to adjust gradually, the mutual alignment of nitrile groups to form a stronger dipolar interaction. In this case, some molecular chains will pack into a molecular rod in the amorphous region, as evidenced by the  $L_c$  (100) increase (Table II). Although prestretching increased the preferred orientation along the fiber axis, it did not induce the inactive, helical molecules into the proper position to take cyclization; at higher temperatures (190–210°C), cyclization was first initiated in the amorphous phase. The crystallite size showed a decreasing trend (shown in Table III), implying that cyclization may have occurred in the boundary of the crystalline region, perhaps in the newly formed ordered portion, which was more or less flexible. Stretching imposed a favoring effect; that is, it led to the rearrangement of molecular chains to trigger cyclization with the help of heat; however, at high temperatures (210–230°C), the chains vibrated and rotated rapidly to incur cyclization even without stretching. In this case, the act of stretching barricaded the rearrangement of molecular chains to slow down the initiation of cyclization.

**TABLE V**  
Effect of Tension on Crystalline Structures during Stabilization Between 210 and 230°C

Sample code	Tension (N)	$d$ (100) (Å)	$L_c$ (100) (nm)	$L_c$ (002) (nm)	AI (%)
a	1.0	5.2823	75.00	69.05	42.52
b	1.5	5.3201	21.14	69.07	40.27
c	2.0	5.3169	51.96	77.08	26.85
d	2.5	5.3296	30.69	77.46	29.69



**Figure 6** Effect of tension on the tensile strength of the final carbon fibers.

#### Effect of tension on the tensile strength of the resultant carbon fibers

The treated fibers were further heated in air at the same conditions for full stabilization. The stabilized fibers were then carbonized in nitrogen up to 1250°C. The values of tensile strength are given in Figure 6. The results show that stretching before stabilization led to an abrupt increase in the tensile strength of the final carbon fibers, whereas the tension at high temperatures contributed to only a small increase. Although the reason is not well understood, we inferred that this was due to orientation along the fiber axis. Stretching affected the molecular chains (especially in the amorphous region) to obtain an oriented structure. Therefore, the structure made chain scission and the loss of molecular alignment occur only to a minor extent so that high-strength carbon fibers could be produced. The small contribution in the tensile strength for stretching at high temperatures may have been due to the structures being fixed by stabilization.

#### CONCLUSIONS

Cyclization was initiated first in the amorphous region and then propagated to the boundaries of the ordered phase. At high temperatures, the reactions developed to the crystalline regime.

A tentative mechanism of tension was proposed. The molecular chains in the amorphous region were first affected by stretching, which led the molecular chains in the disordered region to pack into ordered structures. At higher temperatures, stretching played a favoring effect on cyclization with the help of heat. At temperatures high enough to vibrate and rotate themselves, the stretching imposed a depressing effect on the initiation of cyclization.

Stretching before stabilization resulted in an abrupt increase in the tensile strength of carbon fibers, whereas stretching at high temperatures only led to a small increase.

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