

Evolution of Tension During the Thermal Stabilization of Polyacrylonitrile Fibers Under Different Parameters

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ABSTRACT: Complicated physical and chemical reactions can occur during the thermal stabilization of polyacrylonitrile (PAN) fibers, and they can be macroscopically reflected by the evolution of tension in the fibers. In this work, PAN fibers were oxidized under different parameters in a continuous production line. The tension in the fibers was examined in detail and found to be influenced greatly by the stretching ratio, temperature, and time, as well as the porosity of the PAN precursors. As the thermal stabilization proceeded, tension with different characteristics could result from various reaction mechanisms. At the initial stage, a higher temperature was helpful for lowering the tension, but the tension increased with an increasing

stretching ratio. In a later stage, the tension was dominantly dependent on the cyclization reaction and increased with increasing temperature or time. Under the same stabilization conditions, the tension in low-porosity fibers was higher than that in high-porosity fibers. The microstructures, characterized by high-resolution transmission electron microscopy, provided some direct evidence for the partially stabilized fibers that the stabilization in the crystalline phase was slower than that in the amorphous phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5500–5506, 2006

Key words: fibers; stabilization; tension

INTRODUCTION

Thermal stabilization (also called preoxidation) is a crucial step in the production of polyacrylonitrile (PAN)-based carbon fibers. During heat treatment at ~ 200–300°C, PAN precursors are converted into infusible and nonflammable fibers with a ladder structure suitable for further carbonization.^{1–4} In this process, tension stretching is deemed an essential condition to obtain high-quality carbon fibers and has been paid more attention by a lot of researchers.^{5,6} In 1959, Shindo⁷ first developed the manufacturing technology for PAN-based carbon fibers, but he did not obtain carbon fibers with high tensile strength, mainly because no stretching was applied to the PAN fibers during the thermal stabilization. In 1963, Watt⁸ fabricated new thermal stabilization equipment by which stretching could be achieved via the control of the speed differences between the feed and take-up rollers. He achieved a breakthrough in manufacturing high-quality carbon fibers. At present, numerous studies have also been carried out in this field. It is reported in the literature^{9,10} that prestretching has significant influence on the physical shrinkage of PAN fibers because of the variation of the morphological

order. Bahl and Mathur¹¹ found that an optimum load exists during stabilization, and any underload or overload deteriorates the final tensile strength. Wu et al.⁶ indicated that tension during low-temperature stabilization can lead to a great increase in the tensile strength of carbon fibers, whereas tension at high temperatures results in only small improvements.

By far, most of the previous work has been confined to the effect of stretching on the properties of the resultant carbon fibers, whereas this work mainly discusses the causes and factors related to the tension. The influence of thermal stabilization parameters, such as the temperature and time, and the properties of precursors on the tension in fibers has been investigated to provide a better understanding of the tension mechanism, to optimize the thermal stabilization process, and to improve the mechanical properties of the resultant carbon fibers.

EXPERIMENTAL

Precursors

Three PAN fiber tows (named P1, P2, and P3) were selected as precursors. The fibers, with 1000 filaments in each tow, were wet-spun in dimethyl sulfoxide with a copolymer of acrylonitrile and itaconic acid. The properties of the precursor fibers are listed in Table I.

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TABLE I
Properties of the Precursor Fibers

Precursor	Titer (dtex)	Tensile strength (cN/dtex)	Elongation at break (%)	Porosity (%)	Density (g/cm ³)
P1	1.05	8.81	10.8	2.32	1.176
P2	1.08	8.31	11.4	2.90	1.174
P3	1.05	7.10	11.2	4.10	1.170

Thermal stabilization

A self-designed continuous production line (illustrated in Fig. 1) composed of two furnaces and six sets of stretching rollers was used for thermal stabilization. Each furnace had five separate temperature zones and could be set to different temperatures. In this study, PAN fibers were preoxidized in air with stepwise temperature settings, and stretching was imposed through the control of the speed differences between the feed rollers and the take-up rollers. The fibers between rollers I and II and rollers II and III were stretched at a specific ratio, whereas the fibers between III and IV were kept at a constant length. To investigate the effects of different parameters on the tension in the fibers, four separate experiments were carried out. The detailed parameters are listed in Table II:

1. Experiment for the stretching ratio: Three stretching ratio distributions (λ_1 , λ_2 , and λ_3) were used during thermal stabilization. Precursor P1 was passed successively through 10 temperature zones, which were set to temperature setting T_a at the speed of 0.3 m/min.
2. Experiment for the temperature: Two temperature settings (T_a and T_b) were designed to oxidize the same precursor fiber (P1). In each process, the feeding speed was 0.3 m/min, and the stretching ratio distribution was λ_2 .
3. Experiment for the time: Running speeds V_1 (0.3 m/min) and V_2 (0.2 m/min) were selected to feed the same precursor fiber (P1). The residence times in each temperature zone were 8 and

13 min, corresponding to V_1 and V_2 . The temperature setting was T_a , and the stretching ratio distribution was λ_2 .

4. Experiment for the precursor: Precursor fibers P1, P2, and P3 were simultaneously oxidized at the speed of 0.3 m/min. The temperature setting was T_a , and the stretching ratio distribution was λ_2 .

As illustrated in Figure 1, two thermal stabilization furnaces were designed to separate from each other, and the fibers from one temperature zone to another passed through an ambient-temperature region as a matter of convenience for sampling the fibers oxidized at different temperatures and for rapidly cooling the fibers to the ambient temperature. In this way, the microstructures and properties of these fibers after each thermal stage could be largely maintained for further characterization.

Carbonization

After thermal stabilization, the oxidized fibers were subjected to low-temperature carbonization in a pure nitrogen atmosphere (purity = 99.9999%) from 350 to 600°C under a 1.5% stretching ratio, and this was followed by high-temperature carbonization also in a pure nitrogen atmosphere from 1200 to 1400°C under 4% shrinkage to obtain the resulting carbon fibers.

Characterization of the PAN precursor fibers

An XD-1 fineness tester and XQ-1 strength and elongation tester (both made at Donghua University,

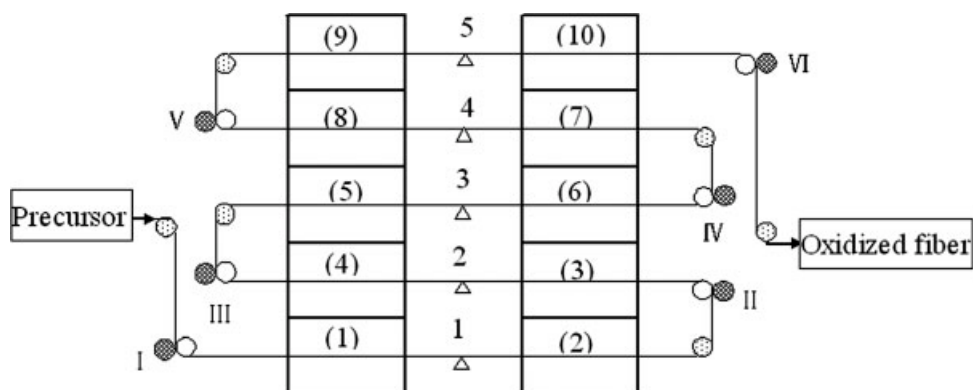


Figure 1 Schematics of the continuous thermal stabilization production line: [(1)–(10)] temperature zones, (I–VI) stretching rollers, and (1–5) tension testing points.

TABLE II
Parameters of Thermal Stabilization

	Temperature zone									
	1	2	3	4	5	6	7	8	9	10
T_a (°C)	194	203	221	232	240	246	251	262	269	274
T_b (°C)	211	219	232	241	245	249	255	262	270	274
Tension testing point	1		2		3		4		5	
λ_1 (%)	0		0		0		0		0	
λ_2 (%)	2.0		0		0		0		0	
λ_3 (%)	3.4		2.6		0		0		0	

Shanghai, China) were used to measure the titer and tensile properties, respectively, of the PAN precursor fibers at room temperature. The tensile properties of single filaments were measured at a crosshead rate of 5 mm/min and a gauge length of 20 mm under a load of 10 g. In each case, at least 30 filaments were tested to obtain the average values, as tabulated in Table I.

The density of the precursor fibers was obtained at 25°C by a density gradient column method in a mixture of *n*-heptane and carbon tetrachloride with a gradient from 1.00 to 1.60 g/cm³.

The porosity (P) of the precursor fibers was measured with a density method and calculated with eq. (1):

$$P = \frac{\rho_0 - \rho}{\rho_0} \quad (1)$$

where ρ_0 is the standard density of PAN homopolymer fibers and ρ is the measured density of copolymer precursor fibers.

Tension determination

A DXF-400 tension tester (Germany) was used to measure the tension in the fibers on line. Five testing points, marked as triangles, are illustrated in Figure 1.

Fourier transform infrared (FTIR) analysis

FTIR measurements were conducted through the loading of samples on KBr disks (0.5-mg sample mixed with 200 mg of KBr) on a Bruker Vector 22 spectrometer (America). The sample fibers were obtained from the production line after being treated at different temperatures.

High-resolution transmission electron microscopy (HRTEM) analysis of the microstructure

The microstructure of the stabilized fibers was observed with a Tecnai 20 II-Twin high-resolution transmission electron microscope at an accelerated voltage of 200 kV. Fibers were embedded in an epoxy resin and solidified at 60°C. Transverse sections thinner than 30 nm were cut on a Reichert-Jung ultrami-

crotope with a diamond knife and collected on Formvar-coated 400-mesh copper grids.

Mechanical properties

The tensile strength of the resulting carbon fiber tows (1000 filaments) was measured on an RGD-5 tensile-testing machine (Shenzhen, China). According to the National Standard of the People's Republic of China (GB 3362 ~ 3366-82), the carbon fiber tows were impregnated with an epoxy resin, dried at 120°C, and cemented on both ends onto paper cards. The tensile strength was measured at a crosshead rate of 5 mm/min and a gauge length of 200 mm. An average strength was ultimately achieved by the measurement of 20 samples.

RESULTS AND DISCUSSION

Effect of the stretching ratio on the tension in the fibers

The changes in the tension in the fibers under different stretching ratios are shown in Figure 2. When the stretching ratio distribution is λ_1 , the fibers are kept at

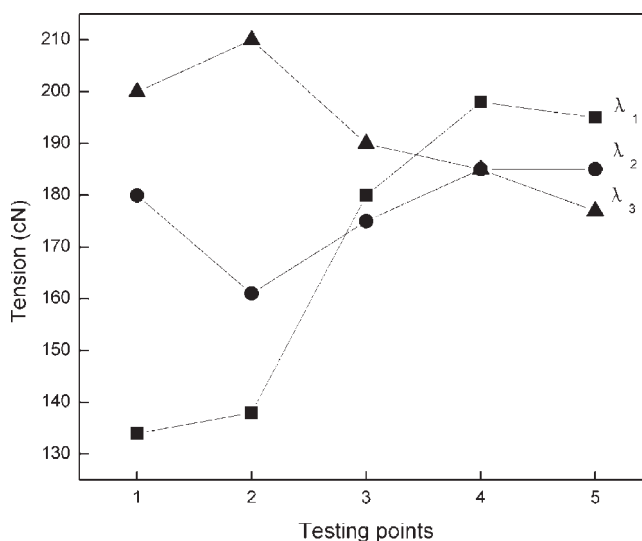


Figure 2 Effect of the stretching ratio on the tension in PAN fibers.

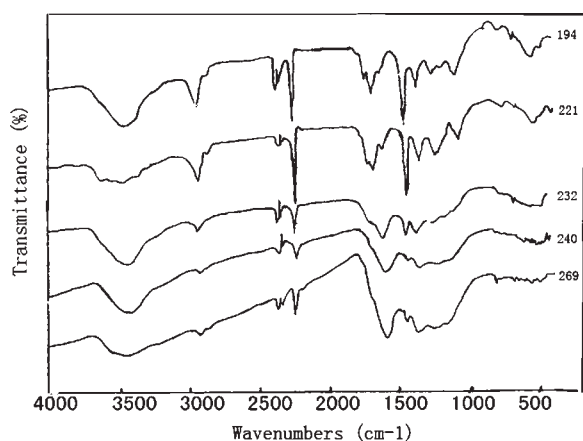


Figure 3 FTIR absorbance spectra of PAN fibers stabilized at different temperatures.

a constant length during the whole preoxidation process. The tension is rather low at the initial stage. As the temperature increases, the tension increases rapidly until a stable value is achieved. When the stretching ratio distribution is λ_2 , the tension is high at the initial stage because of stretching by 2.0%, but it decreases remarkably after the stretching is removed at testing point 2, and then it increases gradually at the subsequent testing points. However, the tension of λ_2 is still higher than that of λ_1 at testing point 2. When the stretching ratio is λ_3 , the tension is very high at the initial stage because of stretching by 3.4 and 2.6% successively. However, the tension decreases markedly with the stabilization proceeding. The aforementioned results indicate that there are different tension mechanisms between the initial stage and the later stages during thermal stabilization. At the initial stage (below ca. 230°C), PAN molecular chains are in a rubbery state with severe Brownian motion, which leads to physical shrinkage of the fibers. This shrinkage results only in low tension in the fibers, whereas stretching has a significant influence on the tension in this period. If the stretching ratio is moderate, the tension generated will be fairly high because of the internal stress accumulating (see the tension of testing point 2 in curve λ_2). However, if the stretching ratio is excessive, the tension will decrease in the following process (illustrated in curve λ_3). During the later stages (after about 230°C), cyclization, dehydrogenation, and oxidation reactions take place to convert PAN molecular chains from a straight structure to a ladder structure,¹² as confirmed by FTIR spectra shown in Figure 3. The IR spectra show no obvious changes below 230°C, whereas above 230°C, the absorption band at 2243 cm^{-1} assigned to the nitrile group and the band at 2930 cm^{-1} assigned to C—H weaken, but the band at 1590 cm^{-1} assigned to C=N and the band at 1363 cm^{-1} assigned to C=C intensify, demonstrating that the fiber shrinkage mechanism

changes from physical shrinkage to a chemical one above 230°C. As a result, thermal stabilization reactions become the main factor for the tension in the fibers. With the reaction proceeding, the internal stress resulting from chemical shrinkage becomes higher and higher, giving rise to the increase in the tension, as shown in curve λ_1 and curve λ_2 . On the contrary, the tension in curve λ_3 decreases, and this is probably due to two reasons. On the one hand, some of the internal stress may be released by the removal of the outer force field; on the other hand, overstretching in the initial stage leads to high internal stress in the fibers, which will accumulate during further thermal stabilization. When the fibers are oxidized at a high temperature, intense chemical shrinkage will take place. Under both effects, chain scission may appear locally, and the tension in fiber will decrease as a result.

Effect of temperature on the tension in the fibers

The changes in the tension at different temperature settings (T_a and T_b) are shown in Figure 4. For each temperature zone, the temperatures of T_b are no lower than those of T_a . The temperature differences are 0–17°C between the corresponding zones (listed in Table II). When the temperature is below 230°C, the tension for T_b is lower than that for T_a at testing point 1, whereas it is reversed when the temperature is above 230°C at testing points 2–5. Because the tension is a reflection of the physical and chemical reactions during thermal stabilization, different reaction mechanisms should be responsible for the tension changes between the initial stage and the later stages. Gupta and Harrison¹³ indicated that thermal stabilization reactions initiated in the amorphous part of a

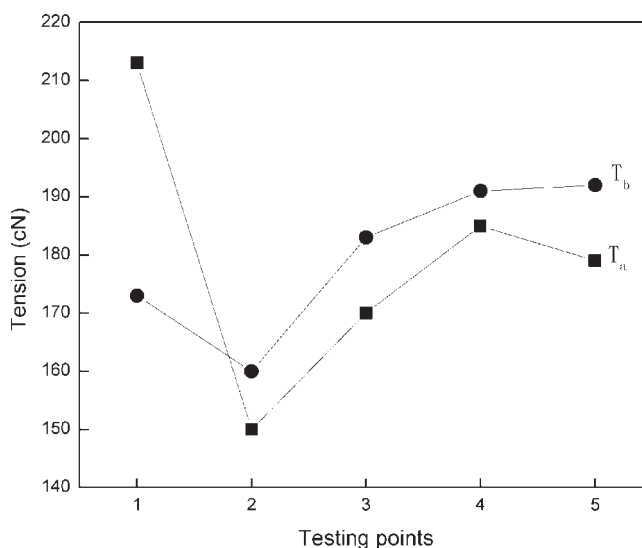


Figure 4 Effect of the preoxidation temperature on the tension in PAN fibers.

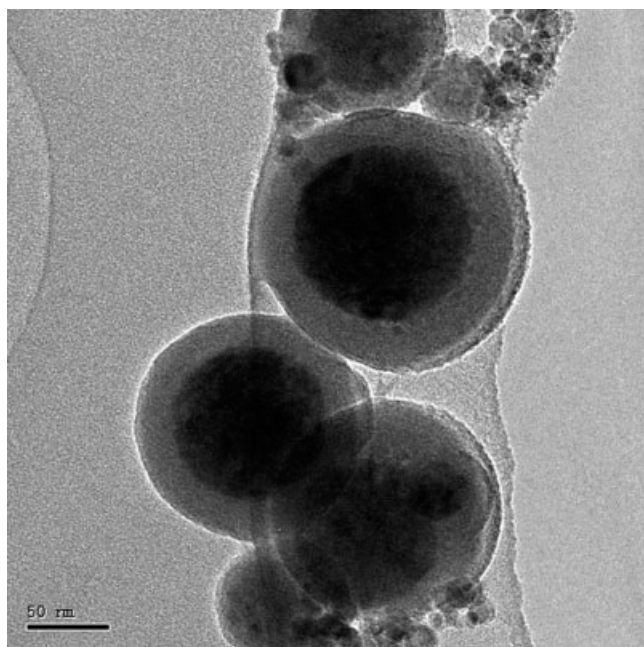


Figure 5 HRTEM morphology of partially stabilized fibers.

copolymer at temperatures below 200°C contributed the major portion of macroscopic shrinkage. Reactions propagated to crystalline components at higher temperatures. Wu et al.¹⁴ analyzed the nitrogen concentration in preoxidized fibers by X-ray photoelectron spectroscopy and also proposed that the cyclization first proceeded in an amorphous region (before 230°C) and then occurred in a crystalline region, resulting in an increase in the N concentration in the fiber surface at first and a sudden decrease later. They further found by FTIR and wide-angle X-ray diffraction experiments that the crystalline morphology was largely reserved in the initial stage, with a considerable number of nitrile groups markedly vanishing.⁶ An analysis of the orientation of the crystalline region also showed an initial rigid structure and a subsequent relaxed structure during stabilization. In this work, the two stabilization reaction mechanisms can be described by a new index: the tension in the fibers. According to ref. 13, the PAN structure is composed of laterally ordered domains and disordered (or amorphous) domains. The disordered domains, which consist of entanglements, chain ends, defects, and comonomer sequences, have a relatively loose structure and some free space. Therefore, it is easier for the C—C bond to rotate and for chain segments to move. Consequently, the rearrangement of PAN molecular chain segments occurs preferably in an amorphous domain below about 230°C, preparing for the cyclization of nitrile. In this period, a higher temperature is helpful for enhancing the molecular motion ability, and this makes it much easier for molecular chains to orient along the fiber direction. Therefore, the tension

in the fibers is lower at higher temperatures below 230°C. Above 230°C, a higher temperature is helpful for cyclization and conjugation reactions in a crystalline domain, resulting in larger chemical shrinkage stress. Besides that, the motion of chain segments is suppressed by the dense structure in the ordered region. As a result, the tension is higher at higher temperatures.

As stated previously, the tension in fibers is a macroscopic exhibition of physical and chemical reactions during thermal stabilization. The tension evolution reflects the two stabilization reaction mechanisms proposed by some researchers using other methods. This can be verified further by an HRTEM examination of the oxidized fibers: the stabilization reactions initiate in an amorphous domain in the initial stage, and the reactions propagate to ordered domains in a later stage. The HRTEM microstructures of partially stabilized fibers are shown in Figures 5 and 6. Figure 5 presents typical quasicrystal grains in stabilized fibers. A lot of larger core-shell spheres can be clearly observed. From the magnified image in Figure 6, it is apparent that the shell is amorphous and the core is crystalline with clear fringe lattices. The structure difference in the core-shell structure indicates that large crystallites in PAN fibers give rise to the inhomogeneity of the microstructure in the stabilized fibers, and this may produce a bad effect on the resulting carbon fibers.

Effect of time on the tension in the fibers

Figure 7 shows the changes in tension at a higher running speed (V_1) and a lower running speed (V_2). The

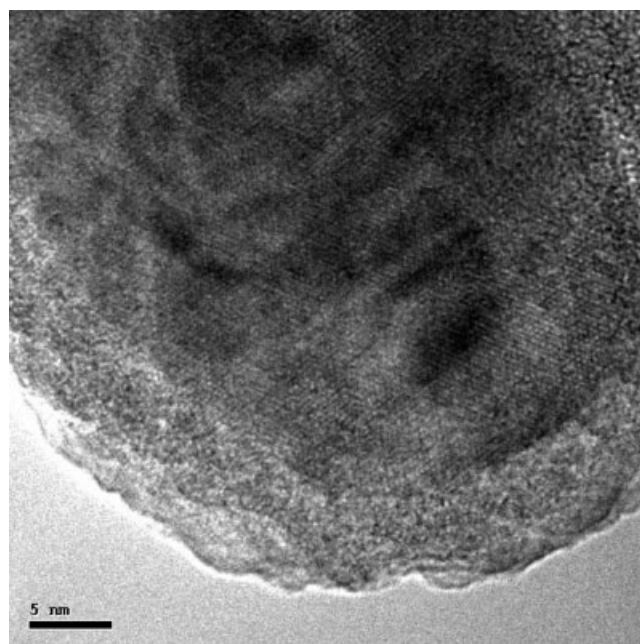


Figure 6 Magnified image of Figure 5.

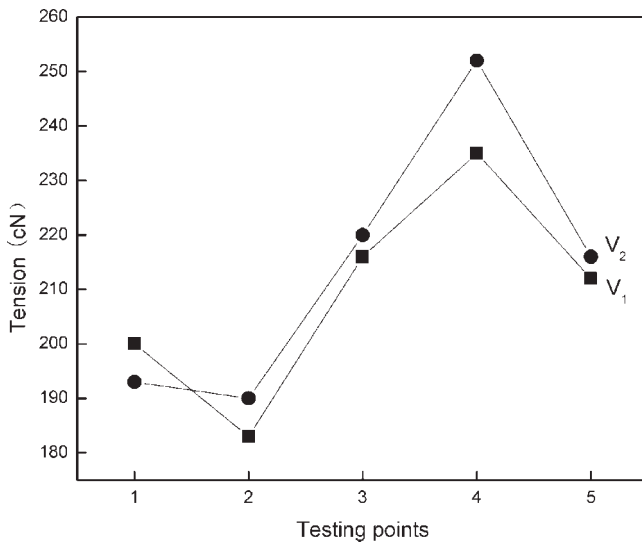


Figure 7 Effect of the stabilization time on the tension in PAN fibers.

trend of the curves in Figure 7 is very similar to trend in Figure 4. In the initial preoxidation stage, the tension at V_2 is lower than that at V_1 , whereas in the later stages, the tension at V_2 is higher than that at V_1 . This indicates that the longer preoxidation time brings lower tension below 230°C , but it is reversed above 230°C . The results in Figures 4 and 7 show that time and temperature have the same effect during the thermal stabilization of PAN fibers. Accordingly, the temperature can be properly increased to shorten the preoxidation time to improve the efficiency of production.

Effect of the precursor porosity on the tension in the fibers

Generally, precursor fibers with a large titer often produce higher tension under the same preoxidation conditions. However, it is very interesting that this is not always correct in those precursors with different properties. Figure 8 illustrates the tension evolution in fibers P1, P2, and P3, which were stabilized simultaneously under the same parameters. Their titers are 1.05, 1.08, and 1.05 dtex, respectively. It is clear that the tension in the fibers has no direct relationship with the titer. Although P2 has the largest titer, the tension in P2 is not the highest. The tension in P1 is much higher than that in P3 even though they have the same titer. Therefore, it can be speculated that as for different precursors, some properties other than titer may be the essential factor of tension during thermal stabilization. Here, to investigate the influence of other properties on tension, the ratio of tension to titer is considered more suitable to be used as an index than tension itself.

Figure 9 shows the ratio of tension to titer for P1, P2, and P3, and the properties of the precursor fibers

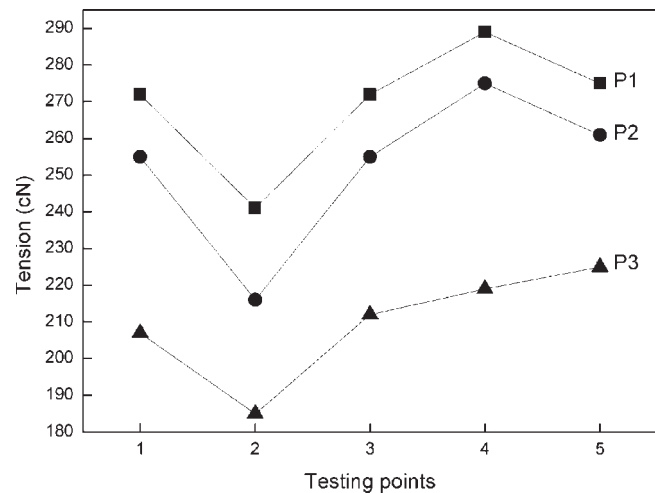


Figure 8 Tension changes in fibers with different titers.

are listed in Table I. The porosity is the key difference that decides some of the other properties of the precursors. Low porosity contributes to high density and high tensile strength of the precursor fibers, whereas high porosity leads to low density and low tensile strength. As for high-porosity precursor fibers, the loose structure may supply more space and make it easier for the cyclization of nitrile, which will generate less stress in the fibers. Moreover, the defects can absorb and release part of the internal stress and result in stress relaxation. Therefore, P3 shows the lowest ratio of tension to dtex, P2 is next, and P1 is the highest. This indicates that the ratio of tension to titer is in inverse proportion to the porosity of the precursor fibers. That is, the higher the porosity is, the lower the ratio of tension to titer is. Accordingly, when parameters for the thermal stabilization of PAN fibers are chosen, the porosity of the precursor fibers must

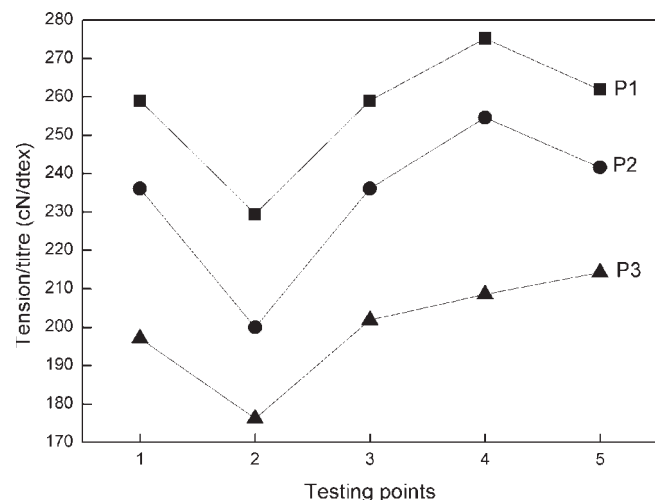


Figure 9 Tension/dttx ratio for fibers with different porosities.

TABLE III
Effects of the Stabilization Parameters on the Tensile Strength of the Carbon Fibers

Process	Temperature settings	Total stabilization time (h)	Total stretching ratio (%)	Precursor fiber	Tensile strength of the carbon fibers (GPa)
1	194–203–221–232–240–246–251–262–269–274	2.0	3.5	P1	3.53
				P3	3.23
2	194–210–221–232–240–251–262–265–269–281	2.6	0	P1	3.12
				P3	3.05
3	194–203–221–232–240–246–251–262–269–270	1.5	8.5	P1	2.96
				P3	2.75

be taken into consideration. Different precursors should use different parameters. As for low-porosity precursors, it is unfavorable to impose a large stretching ratio in fear of chain scission occurring during pre-oxidation. In addition, plasticizers such as dimethylformamide¹⁵ and succinic acid¹⁶ may be used in post-spinning treatments to reduce the dipole interaction and facilitate the stretching of fibers.

Optimization of the thermal stabilization process

According to a study on the tension evolution of PAN fibers, temperature, time, and stretching are the three important parameters in thermal stabilization; they interplay and coaffect the tensile strength of the resultant carbon fibers. Moreover, excellent PAN precursor fibers are essential for producing higher quality carbon fibers. An excessively high temperature or long time, improper settings of stepwise temperatures, and stretching overload will all deteriorate the properties of carbon fibers. The parameters must match those of the precursor fibers. Table III shows the effects of different parameters of thermal stabilization on the tensile strength of carbon fibers. All the stabilized fibers were subjected to carbonization under the same conditions. From the results, process 1 is deemed to be most optimal for producing high-tensile-strength carbon fibers.

CONCLUSIONS

The tension evolution during the thermal stabilization of PAN fibers is a reflection of different mechanisms between the initial stage and a later stage. In the initial stage, stabilization reactions initiate in an amorphous

domain. A higher temperature helps to lower the tension in the fibers, whereas the tension increases with an increasing stretching ratio. At the later stage, the reactions propagate to ordered domains. The tension increases with increasing temperature or time.

The initial stretching ratio has a significant effect on the later tension in the fibers. If the fibers are overstretched in the initial preoxidation stage, chains scission may occur in the later period and lead to a reduction of the tension.

Under the same thermal stabilization conditions, the porosity of the precursor fibers is the main factor influencing the tension. Fibers with low porosity usually produce higher tension than those with high porosity.

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