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Effect of stretching on the orientation structure and reaction behavior of PAN fiber during the thermal stabilization

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Abstract

The evolution of structures and properties of Polyacrylonitrile (PAN) precursor fiber during the thermal stabilization was directly related to the mechanical properties of carbon fiber. In the present study, the effects of stretching on the orientation structure and reaction behavior of PAN fibers at different thermal stabilization stages were experimentally investigated. The multi-dimensional structural characterization and mechanical properties tests were used, such as XRD, FT-IR, ¹³C-NMR, Raman and material testing machine, etc, which would help to reveal the evolution mechanism of the microstructure and reaction behavior of PAN fiber during the thermal stabilization. The results showed that in the process of thermal stabilization, stretching caused the rearrangement of crystalline orientation structure, promoted the cyclization reaction process at higher temperature (>200 °C), and furthermore promoted the formation of oriented aromatic like lamellar structure. It can be found that when the drawing ratio of 10% and the exposed temperature at 200 °C were applied to the PAN fiber, the increasing of crystalline orientation was obvious and more aromatic lamellar structures generated. Based on the above process technology, the carbon fiber with the higher graphitization degree and better mechanical properties was finally obtained.

1. Introduction

Polyacrylonitrile (PAN) based carbon fiber is a kind of high performance fiber with the excellent mechanical properties, which was attributed to the graphite microcrystalline structure with highly ordered arrangement along the fiber axis. It is found that in the preparation process of carbon fiber, the controlling of orientation [1–3] as well as the growth and perfection of graphite microcrystalline structure [4–6] are significant to improve the axial mechanical properties of carbon fiber. In this process, the moderate tension stretching is considered as a necessary method.

For PAN–based carbon fiber, the transformation process from the organic polymer structure to the inorganic graphite structure is complicate. The effect difference of stretching on the structural evolution of PAN fiber at each preparation stages is significant. This would affect the formation and orientation of the graphite microcrystalline structure during carbonization process, thus affecting the mechanical properties of the final carbon fiber.

It was found that in the preparation process of PAN precursor, the multi-stage drawing can effectively promote the preferred orientation of PAN molecular chains along the fiber axis and led to the increase of
crystallinity, grain size and orientation degree. And the performance of the PAN precursor was better [7, 8]. Furthermore, in the thermal stabilization stage, the original linear polymer chains of PAN precursor gradually cross-linked to form the trapezoidal structures, which provided the structural platform for the subsequent carbonation reaction to form the ultimate structure of carbon fiber. It was found that the structure of the fiber changed obviously due to the cross-linking reaction and thermophysical shrinkage of PAN molecular chain, which affected the macro shrinkage of the fiber. Wu et al [9–11] found that in the process of thermal stabilization, fibers underwent a two-stage of shrinkage, which included the physical shrinkage and chemical shrinkage, respectively. Many external fields, such as heat treatment temperature and time [12–14], aggregation structure [15–17], copolymerization composition of PAN fiber [18–20], high order structure and formed structure [21, 22], had significant effects on the thermal shrinkage of fiber. Therefore, it is considered that the stretching during the thermal stabilization process can control the relaxation of PAN molecular chain and reduce the depolarization. Further research shows that the stretching during the thermal stabilization process had almost no effect on the variation of element content, while it had a significant influence on the crystalline structure and tensile strength of the fiber [23–25]. Plenty of studies have been carried out on how to match the stretching and the thermal stabilization temperature to improve the performance and quality of the final carbon fiber. However, there were still some unsolved mechanisms, such as how does stretching affect the structural evolution and chemical reaction process of thermally stabilized fibers? What effect does it have on the growth of graphite microcrystalline structure during further carbonization?

In the previous study, it was found that the thermal reaction process was affected by the original aggregation structure of PAN fibers [26–28]. With the further study, it was found that the orientation structure of PAN precursor had a significant effect on the process of thermal stabilization reaction, the formation and evolution of characteristics structure, and thereby influenced the stress–strain performance of the thermally stabilized fibers [29, 30]. Based on the previous research results, the effects of stretching on the orientation structure and thermal stabilization reaction of PAN fibers during the thermal stabilization stage were further studied by means of the multi-dimensional structural characterization and mechanical properties tests, such as XRD, FT-IR, 13C NMR, Raman and Instron machine testing. In the process of thermal stabilization, with the change of fiber aggregation structure, the effects of stretching at different time and temperature stages on the reorientation structure of PAN fibers, the process of thermal stabilization, the formation and evolution of new structure, and the growth of microcrystalline structure of graphite carbide were studied. The effect mechanism of the stretching on the structures and properties of PAN carbon fiber during the thermal stabilization process was also revealed. It will provide a theoretical basis for the design, control and preparation of high-performance PAN based carbon fibers.

2. Materials and methods

2.1. Raw materials and sample preparation

In the present paper, the wet spinning process was adopted to produce the PAN precursor fiber in the laboratory. It was noted that the precursor structure was composed of the acrylonitrile copolymer and itaconic acid, and the content of itaconic acid was less than 1%.

The continuous preoxidation furnace was adopted to realize the peroxidation process of PAN precursor fiber and its schematic diagram was shown in figure 1. The peroxidation temperature and time in each stage were shown in table 1, including a six-step process procedure. Furthermore, the details at different drawing stages were shown in table 2. As seen, the heat-treated temperature, time and drawing ratios before entering furnace and in the furnace were applied to the PAN precursor fiber to realize the peroxidation process. After the peroxidation process, carbon fibers were prepared from the thermally stabilized samples through the carbonization process at 1350 °C for 1 min without the drawing rate. When the carbonization process was finished, the carbon fibers were obtained to use for the subsequent structural and performance evaluations.

2.2. WARD tests

WAXD measurements were performed with a D/max-2550 PC XRD (Japan Science Corporation, Cu Kα, wavelength λ = 1.5406 Å) diffractometer. The x-ray generator operated at 40 kV and 250 mA. The variations in crystallinity and crystallite size of PAN fibers before and after the thermal process were calculated using equation (1) [31] and equation (2) [32].

\[ X_{cry} = \frac{S_{cry}}{S_{amorphous} + S_{cry}} \times 100\% \] (1)

where \( X_{cry} \) represents the crystallinity of PAN fiber, \( S_{cry} \) and \( S_{amorphous} \) are the peak integrated intensities of the crystalline component and amorphous phase, respectively.
\[ L_{(a)} = \frac{K\lambda}{\beta \cos \theta} \]  

where \( L_{(a)} \) represents the crystallite size along the axes of PAN fiber. \( \beta \) is the half-width of the 100 diffraction peak at \( 2\theta \) (16.9°), \( K \) is a constant (0.89), \( \lambda \) is the wavelength of the Cu K\( \alpha \) radiation, and \( \theta \) is the Bragg angle of the 100 diffraction.

\[ f_{cry} = \frac{180 - \sum H_i}{180} \times 100\% \]

where \( f_{cry} \) is the orientation factor of the crystal region and it is the FWHM of the i peak in the azimuthal scanning x-ray diffraction pattern [33].

### 2.3. FT-IR spectroscopy

The infrared spectra of thermal stabilized PAN fiber was analyzed with 5700 Fourier Transform Infrared Spectrometer produced by Nicolet Company. The tabletting method was adopted through adding the KBr. The infrared spectra were obtained with resolution of 16 cm\(^{-1}\) in the wavelength range 400 ~ 4000 cm\(^{-1}\). The relative cyclization rate (RCI) was calculated by equation (4) [34].

\[ RCI = \frac{I_{1620}}{I_{240} + I_{1620}} \times 100\% \]
where $I_{1620}$ represents the intensity of absorption peak, which was attributed to the stretching vibration mode of $\text{C} \equiv \text{N}$ group at 1620 cm$^{-1}$; $I_{2240}$ indicates the absorption peak was related to the stretching vibration mode of $\text{C} \equiv \text{N}$ at 2240 cm$^{-1}$.

### 2.4. $^{13}$C-NMR tests

$^{13}$C-NMR tests (Bruker AV-300 solid state high resolution nuclear magnetic resonance) were adopted to characterize the structural transition of PAN precursor skeleton during the thermal stabilization. The test procedure was as following: the resonance frequency was 73.5 MHz, the pulse width was 6.6 $\mu$s, the cumulative scanning times was 300 $\sim$ 3175 s, and the cycle delay time and contact time were 5 s and 3 ms, respectively. The CP/MAS probe with the diameter of 4 mm was used in the tests, and the rotor rotation rate was 8.5 kHz. From the tests, RCS was defined as the relative content of typical carbon structure and was calculated by equation (5).

$$ RCS = \frac{I_a}{I_{\text{C}=\text{N}} + I_{\text{C} \equiv \text{N}}} $$

(5)

where $I_a$ represents the characteristic peak intensity of skeleton carbon atom in the $^{13}$C-NMR spectrum; $I_{\text{C}=\text{N}}$ represents the intensity of the characteristic peak of $\text{C}=\text{N}$ at 121 ppm; $I_{\text{C} \equiv \text{N}}$ represents the intensity of the characteristic peak of $\text{C} \equiv \text{N}$ at 153 ppm.

### 2.5. Raman analysis

RM2000 micro confocal Raman spectroscopy (U.K.) was used to characterize the graphite structure of carbon fiber. Argon ion laser wavelength was 514.5 nm and Raman shift range were 800 $\sim$ 2000 cm$^{-1}$. The microscopic scan size was greater than 1 $\mu$m and the resolution is 1 cm$^{-1}$. The objective lens was 20X and the diameter of laser spot was 5 $\mu$m. Small bundles of carbon fibers were fixed on a glass slide and then were put into a test chamber followed by the measurement with adjusting the laser spot along the fiber axis.

### 2.6. Tensile properties

The tensile properties of PAN monofilaments after the carbonization process were tested by universal material testing machine (SHUMADZU AG-1S). The length of the monofilament was 20 mm and the stretching speed was 2 mm min$^{-1}$. The average value of 25 samples was taken for each condition. The characteristic mechanical property parameters were calculated by the typical stress-strain curves.

### 3. Results and discussion

#### 3.1. Effect of stretching on the orientation structure of PAN fiber during the thermal stabilization process

With the development of thermal stabilization reaction, linear chains of PAN fiber were gradually transformed into cross-linking structures, which obviously decreased the molecular mobility. In the present study, the different stretching ratios were applied to PAN fiber during the thermal stabilization process. It was found that the effects of stretching at different thermal stabilization stages on the orientation structure of PAN fiber were different. As shown in figure 2, the orientation degree of crystalline region ($f_{\text{cry}}$) for PAN fiber with the drawing ratios was obtained by WAXD. It could be seen that when the heat-treated temperature was within 200 °C, the orientation degree of crystalline region for PAN fiber increased significantly with the increase of heat-treated temperature and drawing ratio. Furthermore, the effect of drawing after heat-treatment at 200 °C for 8 min (drawing ratios were 2%, 6%, and 10%) on the orientation degree of crystalline region was not significant compared with the synchronous effect of heat-treatment and stretching. This was indicated that the mobility and the degree of thermal stabilization reaction were mainly controlled by the heat-treated temperature. It further affected the orientation rearrangement of PAN chains induced by stretching. When the stretching was applied to the PAN fiber at 120 °C, while at this time, the thermal stabilization reaction did not start, and the physical movement and rearrangement of PAN linear molecular chains were induced by stretching. Specially, the sub-ordered molecular chains around the crystalline region were more likely to be rearranged under the tension, which led to the increase of orientation degree in the crystalline region, especially for the higher drawing ratio. With the heat-treated temperature increased, the mobility of PAN molecular chains was obviously enhanced, which resulted in the accelerating effect of the stretching on the rearrangement of molecular chains in crystalline region. It can be observed that there was a tendency of $f_{\text{cry},200^\circ\text{C}} > f_{\text{cry},180^\circ\text{C}} > f_{\text{cry},120^\circ\text{C}}$ at the same drawing ratio. On the other hand, when the heat treatment temperature was more than 180 °C, the thermal stabilization reaction started and the cyclization structure generated. It restricted the mobility of PAN molecular segments. Therefore, with the increase of drawing ratio, the growth rate of orientation degree of PAN crystalline region at 180 °C was relatively lower than that of 120 °C. Furthermore, when the heat-treated temperature increased to 200 °C, the degree of thermal stabilization reaction was relatively higher, which led to a lower
growth rate of orientation degree at 200 °C. Even when the heat treatment was conducted at 200 °C for 8 min, the degree of thermal stabilization was relatively high, and the formed cross-linking structure at this time had a larger restriction on the movement of PAN molecular chains. Therefore, the growth rate of orientation degree of PAN crystalline region had no obvious change with the increase of drawing ratio. In summary, owing to the effect from the mobility and orientation degree and rearrangement of PAN chain, the optimal orientation degree of PAN fiber was obtained for the heat-treated temperature of 200 °C and drawing ratio of 10%.

3.2. Influence of stretching on the cyclization reaction of PAN fiber during the thermal stabilization process
In the thermal stabilization process, the stretching affected the rearrangement of orientation structure for PAN fibers, and even further affected the degree of cyclization reaction [30]. In the present study, the relative cyclization rate (RCI) of PAN fiber measured by FT-IR was used to characterize the degree of cyclization reaction with the drawing ratio at different thermal stabilization stages (figure 3). As shown in figure 3(a), after the heat treatment at 180 °C, RCI value decreased with the increase of drawing ratio. Furthermore, it can be observed that RCI of PAN fiber at 180 °C was lower than that of 120 °C at the same drawing ratio. While, when the heat-treated temperature increased to 200 °C, RCI value gradually increased with the increase of drawing ratio, and were more than that of 180 °C. It indicated that the effect of the stretching on the cyclization process was different during the thermal stabilization stages.
Preliminary research found that the progress of cyclization reaction began from the disordered region of PAN molecular chains and then developed into the crystalline region \[29\]. Based on the characteristics of PAN molecular chain, the mutual repulsion of lateral interaction between the adjacent –CN groups on the same chain and the interattraction between the adjacent –CN and α-hydrogen atoms in the neighboring chains, the mobility of PAN molecular segments was restricted. It was considered that the cyclization reaction occurred firstly between the adjacent –CN in the amorphous region when the heat-treated temperature was 180 °C. Due to the mobility of molecular segments, the cyclization degree was low in this stage. With the increase of the stretching ratio, the orientation degree in the crystalline region of PAN fiber increased, and the content of the disordered region decreased, resulting in the decreasing of RCI. For the same drawing ratio, the orientation degree of crystalline region of PAN fiber at 180 °C was higher than that of 120 °C, which brought about a lower RCI. Since the mobility of PAN chains increased with the heat treatment temperature, and the degree of cyclization increased followed by the gradual transition to the oriented molecular chains. At this time, the relatively regular orientation structures were more helpful to promote the full cyclization reaction between the molecular chains. Furthermore, the larger drawing ratio obviously increased the orientation degree in the crystalline region of PAN fiber, leading to the subsequent increase of cyclization degree. In addition, for the same drawing ratio at 200 °C, a larger orientation degree of crystalline region formed compared to 180 °C. When the heat treatment at 200 °C for 8 min, it can be seen the increase of orientation degree of fiber was not obvious with the drawing ratio. Meanwhile, the increase rate of RCI value was moderate.

Figure 4 shows the relative cyclization rate (RCI) of PAN fiber with the drawing ratio of 10% after the treatment in furnace 6#.

Figure 4. Relative cyclization rate (RCI) of PAN fiber with the drawing ratio of 10% after the treatment in furnace 6#.

3.3. Influence of the stretching on characteristic functional groups of PAN fiber during the thermal stabilization process

With the results of $^{13}$C-NMR measurement, the effect of the stretching on the formation of characteristic structure of preoxidized PAN fiber was studied. Figure 5 shows the relative content of typical carbon structure for PAN fiber at different thermal stabilization stages. As shown, with the increase of drawing ratio, the relative content of unreacted –CN structure of PAN molecular chain gradually decreased, and the relative content of –C=N, –C=CH and –C=C gradually increased. For the same drawing ratio, the stretching at 180 °C induced a
significant increase in the orientation degree in crystalline region compared with the stretching at 120 °C, which resulted in the lower content of unreacted –CN structure and higher content of –C=N, –C=CH and –C=C. It had also proved that the stretching during the heat treatment process can promote the development of the oriented structure of PAN fiber, and concomitantly effected the progressing of thermal stabilization.

The difference of relative content of characteristic structure of PAN fiber formed under the stretching at 200 °C and 180 °C during the preoxidation process was compared and shown in table 3. Since the difference of orientation degree in the crystalline region and RCI between the fibers at different temperatures approached gradually at the later stage of thermal stabilization, it indicated that there was no obvious difference in the relative content of –C=N, –C=CH. In comparison, the difference of relative content of –C=C was still relatively remarkable.

The effects of the drawing at different thermal stabilization stages on the relative content of C=C structure of PAN fibers were obtained and shown in figure 6. As shown, with the increase of the drawing ratio, the relative content of C=C characteristic structure increased significantly. Meanwhile, it can be observed that RCS_{C=C-200 °C} > RCS_{C=C-180 °C} > RCS_{C=C-120 °C} for the same drawing ratio. The results showed that the improvement of orientation degree of PAN fiber under the stretching was more helpful to promote the formation of the ordered cyclized dehydrogenation structure between the molecular chains and the cross-linking, which brought about a larger area of aromatic-like lamellar structure. Thus, more C=C structures generated as shown in figure 7.
3.4. Influence of the stretching on the structures and properties of PAN fiber

The graphite structure of PAN carbon fiber after the thermal stabilization under the drawing was characterized by Raman spectroscopy [35], which was shown in figure 8. As seen in figure 8(a), the D band at 1354 cm$^{-1}$ was the stretching vibration peak of sp$^3$ hybrid carbon atoms, which mainly reflected the structural characteristics of the disordered graphite of carbon fibers. While G band at 1580 cm$^{-1}$ was the stretching vibration peak of sp$^2$ hybrid carbon atoms, which reflected the characteristic structure of ordered oriented graphite lamellae of carbon fibers. The graphitization degree of carbon fiber was usually characterized by the relative content ratio (R) of D peak area and G peak area. The smaller the R value was, the higher the graphitization degree was. The half-width (FWHM) at half maximum of G peak was used to characterize the uniformity of graphite structure. The narrower the half-width was, the better the uniformity ordered graphite structure was. Figures 8(b) and (c) show that R value of graphitization degree and FWHM of G peak decreased with the increase of drawing ratio. At the same drawing ratio, R and FWHM of fibers stretched at 200 °C were relatively lower than that of 180 °C. As the lamellar graphite structure of carbon fiber was gradually evolved from the aromatic lamellar structure of thermally stabilized fiber, it was considered that the orientation degree of crystalline region induced by stretching could further promote the formation of large-area aromatic lamellar structure in the system. It was an important factor affecting the relatively higher perfection of graphitized structure generated after carbonization of PAN fiber.

The mechanical properties of PAN carbon fibers prepared from stretching at different thermally stabilized were obtained and shown in table 4. As seen, with the increase of drawing ratio, the orientation degree of crystalline region increased, and the graphitization degree and graphitization uniformity of carbon fibers were relatively higher, which led to a higher tensile strength and tensile modulus. For the same drawing ratio, the stretching at 200 °C could further promote the improvement of the orientation degree in the crystalline region, and this was helpful to improve the tensile strength and tensile modulus of carbon fiber.
4. Conclusions

In the present study, the effects of stretching on the orientation structure and reaction behavior of PAN fibers at different thermal stabilization stages were experimentally investigated. The multi-dimensional structural characterization and mechanical properties tests were conducted to reveal the evolution mechanism of the microstructure and reaction behavior of PAN fiber during the thermal stabilization.

Table 4. Mechanical properties of PAN based carbon fibers with drawing and treatment from furnace 6# then subsequent carbonization process.

| Heat-treated temperature and drawing ratio | Tensile strength (GPa) | Tensile modulus (GPa) |
|-------------------------------------------|-----------------------|----------------------|
| 180 °C(λ = 2%)                           | 3.51                  | 260                  |
| 180 °C(λ = 6%)                           | 3.63                  | 264                  |
| 180 °C(λ = 10%)                          | 3.75                  | 269                  |
| 200 °C(λ = 2%)                           | 3.75                  | 264                  |
| 200 °C(λ = 6%)                           | 3.79                  | 271                  |
| 200 °C(λ = 10%)                          | 3.83                  | 277                  |
1) The effect of stretching on the orientation degree of PAN fiber was different at different thermal stabilization stages. It can be observed that heat treatment at 200 °C and simultaneous drawing was the best way to obtain higher orientation degree.

2) When the heat-treated temperature was 180 °C, the stretching could restrain the cyclization reaction, and the higher the drawing ratio led to the lower cyclization degree. With the further increasing of the heat treatment temperature, the effect of drawing on the cyclization reaction gradually decreased.

3) The stretching during the thermal stabilization process was conducive to form the aromatic lamellar structure in the PAN fiber, which had a significant effect on the graphitization degree. Furthermore, the drawing ratio of 10% and temperature at 200 °C were determined to be the optimal factors to obtain the higher graphitization degree and tensile properties.

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Data availability statement

All data that support the findings of this study are included within the article.

Author Contributions

C.L. and B.W. conceived and designed the experiments; B.W. performed the experiments; B.W., C.L. and W.C. analyzed the data and wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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