Microstructure Evolution of Dry-jet Wet-spinning Polyacrylonitrile Fibers during Oxidative Stabilization

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Abstract. During oxidative stabilization, the chemical structure, crystalline structure and morphological structure of dry-jet wet-spinning polyacrylonitrile fibers have great changes. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to systemically investigate the evolution of chemical structure, crystalline structure and fibril structure. The research suggests that the cyclization reactions of C≡N proceed in the beginning when stabilization temperature is lower than 245 °C, and C≡N transforms into C=N and C=C conjugate structures. The crystalline structure changes obviously, and it can be concluded that the stabilization reactions take place in amorphous region at first and then extend to crystalline region as the stabilization progresses. The fibrils in polyacrylonitrile fibers and stabilized fibers of early stabilization stage were separated by the method of ultrasonic etching. But when temperature was higher than 240 °C, fibrils compactly combined with each other and no separated fibrils appeared.

1. Introduction
Polyacrylonitrile (PAN) based carbon fibers have been widely used in aviation, aerospace and other military and civil industries because of their excellent properties, such as high specific strength, high specific modulus, wear resistance, corrosion resistance and high temperature resistance, etc. Therefore, the production of carbon fibers has been highly valued by all countries in the world.

In the production of PAN based carbon fibers, the stabilization process is an essential and time-consuming process, which plays a decisive role in the structure and properties of the final carbon fibers[1]. Therefore, detailed studies on the microstructure evolution are quite important for optimizing the production techniques and improving the mechanical properties of carbon fibers. However, because of the complicity of chemical changes and structural transformation in stabilization process, also the diversity of stabilization conditions and techniques, the research results are not the same[2-4]. In this paper, the PAN precursor fibers were prepared by dry-jet wet-spinning technique in which the polymer liquid passed through the air layer (about several millimeters to several centimeters) before it entered into the coagulation bath. Dry-jet wet-spinning technique is an efficient spinning technique, which is considered to be the mainstream process of carbon fiber production in the future. In this paper, the evolution of chemical structure, crystalline structure and fibril structure of dry-jet wet-spinning precursor fibers during oxidative stabilization is discussed in order to provide new ideas for the structure research and property improvement of stabilized fibers and support the production of carbon fibers.
2. Experimental

2.1. Materials

The copolymer was polymerized with acrylonitrile (AN) and itaconic acid (IA) (AN/IA 99/1 wt%), using 2, 2′-azobisisobutyronitrile as initiator and dimethylsulfoxide (DMSO) as solvent in nitrogen atmosphere. The polymerization solution was extruded from spinneret cap into air layer, then into coagulation bath to form nascent fibers (dry-jet wet-spinning technique). Then the PAN precursor fibers were obtained by multistep coagulation, preliminary drawing, washing, drawing in boiling water, collapsing, drawing in vapor, heat setting and drying.

2.2. Oxidative stabilization of PAN precursor fibers

PAN precursor fibers (The following is abbreviated as PAN fibers) were stabilized under air atmospheric conditions by gradient elevation of temperature through 220 °C, 230 °C, 240 °C, 245 °C, 245 °C, 255 °C, 255 °C, 255 °C temperature zones in sequence. It took 8 min when the fibers were stretched through each zone, and the stretching ratio was 5%.

2.3. Ultrasonic etching treatment

The fibers heated at different temperatures were cut into pieces about 2 mm and placed in centrifuge tubes respectively, and 90 wt% DMSO aqueous solution was added as the solvent. Then the tubes were put in an ultrasonic cleaner for 30 h with a frequency of 40 kHz and a bathing temperature of 75 °C. After that, the suspension was dropped on a copper mesh covered with carbon film, washed with distilled water and dried naturally for the observation of scanning electron microscopy (SEM).

2.4. Characterization

The chemical structure was analyzed by Bruker Alpha Fourier transform infrared spectroscopy (FTIR). Scanning range was 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹.

X-ray diffraction (XRD) measurements (Rigaku D/max-rc) were made with Ni-filtered, CuKα radiation (λ=0.15418 nm), acceleration voltage 40 kV and current intensity 50 mA. The scanning speed was 3°/min with a scanning step of 0.02° in the range of 5-50°. The crystalline interplanar spacing d and crystallite size (Lc) were calculated from the Bragg equation and the Scherrer equation:

\[
L_c = \frac{K \lambda}{B \cos \theta}
\]

(1)

Where \( \lambda \) was the wavelength of CuKα X-ray, \( \theta \) was the Bragg angle, \( B \) was the full width at half maximum intensity (FWHM) of the peak (100) around \( 2\theta=17° \), and \( K \) was a constant value 0.89.

The crystallinity (C) of fibers was determined by Hinrichsen’s method:

\[
C = \frac{A_c}{A_c + A_a} \times 100\%
\]

(2)

A_c and A_a were the areas of diffraction maximum of crystalline peak and amorphous zone respectively.

The fibrillar morphologies of samples were observed by SU-70 Hitachi field emission SEM with a voltage 1.0-5.0 KV.

3. Results and discussion

The stabilized fibers from ten gradient-elevated temperature zones in sequence are named as B1~B10 from low temperature to high temperature respectively, and the PAN fibers are named as B0. The corresponding relationship refers to table 1.

3.1. Changes in the chemical structure of PAN fibers during stabilization

The FTIR spectra of PAN fibers and stabilized fibers of each temperature zone are shown in figure1. With the increase of stabilization temperature, the absorption peaks of stretching vibration of CH₂ near
2940 cm\(^{-1}\), C≡N near 2240 cm\(^{-1}\), C-CN near 1070 cm\(^{-1}\), and the absorption peaks of bending vibration of CH\(_2\) near 1455 cm\(^{-1}\), respectively, are gradually weakened. The absorption peaks of stretching vibration of C=N and C=C gradually increase with temperature rising; the peak near 800 cm\(^{-1}\) of =C-H functional group also increases with stabilization temperature going higher, and this peak does not appear in oxygen-free atmosphere, so it is inferred that this peak is related to oxygen-induced cyclization aromatization[5]; in the early stage of stabilization, the absorption peaks of stretching vibration of C=O near 1735 cm\(^{-1}\) and C-O near 1155 cm\(^{-1}\) decrease with the increase of temperature, and the latter disappears when the temperature reaches 245 °C.

**Table 1. The stabilization of dry-jet wet-spinning PAN fibers**

| Stabilization of PAN fibers | Shortened names of PAN fibers and stabilized fibers |
|-----------------------------|--------------------------------------------------|
| 25°C                        | B0                                               |
| 220°C                       | B1                                               |
| 230°C                       | B2                                               |
| 240°C                       | B3                                               |
| 240°C                       | B4                                               |
| 245°C                       | B5                                               |
| 245°C                       | B6                                               |
| 245°C                       | B7                                               |
| 255°C                       | B8                                               |
| 245°C                       | B9                                               |
| 245°C                       | B10                                              |

**Figure 1. FTIR spectra of PAN fibers and the stabilized fibers**

The above results show that C≡N transforms into C=N and C=C conjugate structures. From the spectra, it can be seen that the absorption peak intensity of C≡N increases rapidly when the temperature reaches 220 °C and stops increasing when the temperature reaches 245 °C. But the peak intensity of C≡N decreases gradually with temperature rising, which indicates that pyrolysis of C≡N rather than cyclization occurs at the later stage of stabilization due to higher temperature.
vibration absorption peaks of C≡N and CH₂ do not disappear, which indicates that C≡N is only partially cyclized and does not completely convert to C=N structure.

During the whole stabilization process, the absorption peaks of stretching vibration and bending vibration of CH₂ decrease gradually, which shows that dehydrogenation reaction exists in the whole process. The absorption peak of C=O introduced by IA copolymer gradually weakens. In the early stage of stabilization, oxygen combines with carbon in the cyclic structure to form C-O groups. When the temperature is higher than 245 °C, some C-O groups are oxidized and decomposed, escaping in the form of small molecules, thus the intensity of C-O absorption peak weakens or even disappears.

3.2. Evolution of crystalline structure of PAN fibers during stabilization

It was found that there were two distinct peaks of PAN fibers near 2θ≈17° (corresponding to the (100) crystal plane of quasi-hexagonal system) and 2θ≈29° (corresponding to the (110) crystal plane of quasi-hexagonal system) which indicated PAN crystallite structure[6-7].

According to XRD data, the spectra were plotted as figure 2 and the crystalline size and crystallinity of the fibers were calculated as table 2. It is concluded that the crystalline size and crystallinity of the fibers increase gradually in the early stage of stabilization, which are higher than that of the PAN fibers. When the temperature is higher than 230°C, the crystalline size gradually reduces, and the crystallinity gradually decreases when the temperature is higher than 220 °C.

The above results illustrate that some molecular chains in the amorphous region are reorganized orderly in the early stage of stabilization under the action of temperature field and external force field (stabilization stretching). Because of the high interfacial energy, the possibility of ordering transformation of the molecular chains is increased, which leads to the growth of quasicrystalline structure[3]. With the increase of temperature, the crystalline size increases gradually. When the stabilization temperature reaches a certain level, the quasicrystalline structure of the fibers is destroyed by heating, and begins to change to amorphous structure, so the crystalline size and crystallinity decrease gradually. This indicates that the stabilization reaction first takes place in the amorphous region, and gradually extends to the crystalline region with temperature rising.

A new diffuse diffraction peak appears near 2θ≈25.5° in the later stage of stabilization, reflecting the formation of new ordered structure. This peak is the characteristic peak of cyclization and aromatization structure, which indicates that the fiber has changed from linear structure of PAN to ladder structure.
Table 2. XRD data and structural parameters based on figure 2

| Samples | Stabilization temperature (°C) | Crystallite size $L_c$ (nm) | Crystallinity (%) |
|---------|-------------------------------|----------------------------|-------------------|
| B0      | 25                            | 7.6816                     | 67.70             |
| B1      | 220                           | 9.6283                     | 68.29             |
| B2      | 230                           | 10.7415                    | 59.98             |
| B3      | 240                           | 8.8559                     | 51.50             |
| B4      | 240                           | 6.3157                     | 44.11             |
| B5      | 245                           | 6.0881                     | 33.58             |
| B6      | 245                           | 4.6097                     | 28.47             |
| B7      | 245                           | 3.8805                     | 27.22             |
| B8      | 250                           | \                          | \                |
| B9      | 245                           | \                          | \                |
| B10     | 245                           | \                          | \                |

3.3. Fibrillar morphology of PAN fibers and the stabilized fibers

The PAN fibers and their stabilized fibers were etched in 90 wt% DMSO aqueous solution at 75 °C for 30 h. As shown in figure 3 (the direction of the black arrow is the direction of the fiber axis), the separated fibril structure of PAN fibers and the fibers at the early stage of stabilization appears.

Figure 3. Fibrillar morphology of PAN fibers and the stabilized fibers after etched ultrasonically for 30 h (a) PAN fibers; (b) stabilized at 220 °C; (c) stabilized at 230 °C

Figure 3(a) is the morphology of the fibril structure of the end of a PAN fiber. It can be seen that the diameter of the fibrils mostly distributes in the range of 100-200 nm. A few larger size fibrils are considered to be no separation of two or several fibrils. The fibril diameter of dry-jet wet-spinning
PAN fibers is obviously smaller than that of wet-spinning PAN fibers[8]. Figure 3(b) is the morphology of the fibril structure from 220 °C stabilized fibers, and the diameter of the fibrils is also mostly in the range of 100-200 nm. As shown in figure 3(c), the fibrils of a 230 °C stabilized fiber begin to adhere to each other, and after ultrasonic etching, the fibrils are separated, but there are almost no single fibrils. This indicates that the cyclization reaction enhances and the degree of cross-linking between fibrils improves at this temperature. When temperature is higher than 240°C, fibrils compactly combine with each other and no separated fibrils appears. The result is attributed to the improvement of crosslinking reactions among fibrils which brings about a compact combination of fibrils and makes fibrils inseparable[8]. This is consistent with the above results of chemical reaction and crystalline structure evolution.

4. Conclusions
During stabilization, C≡N functional group in PAN fibers transforms into C≡N and C=C conjugate structures. At the later stage of stabilization, C≡N pyrolysis rather than cyclization occurs due to higher temperature. C≡N is only partially cyclized and does not completely convert to C≡N structure. Dehydrogenation reaction exists in the whole stabilization process. When the temperature is higher than 245°C, some C-O groups are oxidized and decomposed, escaping in the form of small molecules.

The XRD results illustrate that some molecular chains in the amorphous region are reorganized orderly in the early stage of stabilization. With the increase of temperature, the crystalline size increases gradually. When the stabilization temperature reaches a certain level, the quasicrystalline structure of the fibers is destroyed by heating. This indicates that the stabilization reaction first takes place in the amorphous region, and gradually extends to the crystalline region with temperature rising.

Under ultrasonic etching, the fibrils of fibers separated, and the diameter of the fibrils is mostly in the range of 100-200 nm. As temperature rising, the fibrils of stabilized fibers begin to adhere to each other which indicates that the cyclization reaction enhances and the degree of cross-linking between fibrils improves. The above three results are consistent.

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