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Evolution mechanism of cyclized structure of PAN-based pre-oxidized fiber during low temperature carbonization process

Bin Wang1, Shuai Wu2,3, Chenggao Li4,5,6,7,∗ and Weiyu Cao1,3,8,*

1 Central Research Institute of Building and Construction Co., Ltd, MCC, Beijing 100088, People’s Republic of China
2 State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, People’s Republic of China
3 The Key Laboratory of Education Ministry on Carbon Fiber and Functional Polymer, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China
4 Key Lab of Structures Dynamic Behavior and Control, Ministry of Education, Harbin Institute of Technology, Harbin 150090, People’s Republic of China
5 Key Lab of Smart Prevention and Mitigation of Civil Engineering Disasters of the Ministry of Industry and Information Technology, Harbin Institute of Technology, Harbin 150090, People’s Republic of China
6 School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, People’s Republic of China
7 Postal address:73 Huanghe Road, Nangang District, Harbin 150090, People’s Republic of China
8 Postal address: Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China
∗ Authors to whom any correspondence should be addressed.
E-mail: mccwangbin@126.com, lichenggao@hit.edu.cn and caowy@mail.buct.edu.cn

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Abstract

The low temperature carbonization process is an important stage to realize the structural transition from the organic cyclized structure of PAN based pre-oxidized fiber to the inorganic pseudo-graphite structure of the ultimate carbon fiber. In the present paper, the evolution mechanism of cyclized structure and aggregation structure of PAN stabilized fiber during low temperature carbonization was studied by means of TGA, 13C-NMR, XRD, XPS and Raman. The results indicated that when the heat-treated temperature was lower than 450 °C, the mainly chemical reactions were the dehydrogenation and pyrolysis reactions in acyclic linear molecular chain or partial cyclized structure. At this stage, the growth of cyclized structure was not obvious. While the original ordered structure was destroyed gradually and the internal stress increased significantly. It induced the cyclized structure to be further oriented. When the temperature was higher than 450 °C, the polycondensation and reconstruction in aromatic heterocyclic structure was more important. The early aromatic heterocycles had many different structural scales, poor homogeneity and many defects in the heterocycles. At this stage, a new pseudo-graphite crystalline structure gradually formed and the d-spacing of graphite layer decreased slightly and crystallites size increased slowly with the increase of heat-treated temperature. When the temperature was higher than 550 °C, the pseudo-graphite base structure gradually formed. The d-spacing were further reduced slightly, and the crystallites size increased slowly. A new ordered basis structure was gradually developed into carbon fiber.

1. Introduction

During the carbonization treatment process, the ring structures of PAN pre-oxidized fiber are transformed into pseudo-graphite structure of carbon fiber. Generally, the carbonization process includes two stages, low-temperature carbonization at 300 °C ~ 700 °C and high-temperature carbonization at 700 °C ~ 1500 °C. During the carbonization process, the ring structure of PAN pre-oxidized fiber underwent the complex pyrolysis and reconstruction, in which the original chemical and physical structures were destroyed. Meanwhile, the smaller cyclized structural units were gradually transformed to the pseudo-graphite structure through the crosslinking, polycondensation and pyrolysis accompanied shrinking significantly [1–3]. As a result, the original
structure of stabilized fiber completely disappeared and a new pseudo-graphite microcrystalline structure was
generated [4].

Previous studies have showed that the high temperature carbonization process of PAN fiber started from the
structure of low-temperature carbonized fiber, which was mainly from the removal of non-carbon elements, as
well as the further growth of carbon micro-crystallites. Finally, a pseudo-graphite structure was formed [5–7].
However, there were few and unclear conclusions on the evolution and development of the cyclized structure
and its aggregation structure in the process of low-temperature carbonization.

Watt et al [8] mainly focused on the small molecular products of pyrolysis for PAN-based pre-oxidized fiber
during the carbonization process. However, it was difficult to trace the overall evolution characteristics of the
cyclized structure for PAN based pre-oxidized fiber [9, 10]. In addition, the evolution model of pseudo-graphite
microcrystalline structure has not been established in the low-carbon process while the aggregation structure of
PAN fiber in this stage was considered to be the chaotic state of transition from stabilized structure of pre-
oxidized fiber to the high-carbon micro-structure [11, 12]. The low temperature carbonization process of PAN
fiber was accompanied by the significant macro-shrinkage. The shrinkage rate changed constantly under the
effect of chemical reaction and physical structure. It was suggested that applying drawing in the carbonization
process was necessary to obtain the high-performance PAN carbon fiber. Stretching in the low-temperature
carbonization process could prevent the disorientation of the fiber molecular chain of cyclized structure [13, 14],
while in high temperature carbonization process, tension loading was beneficial to the growth direction of
crystallites [15–17]. Ma et al [18] showed that applying tension during the carbonization process could improve
the orientation of carbon crystallites and mechanical properties, while the excessive tension would reduce the
orientation of the fiber and resulted in the decrease of the tensile strength of carbon fiber. However, in the
carbonization process, the evolution of characteristic structure, which was suitable for stretching and conducive
to the final carbon microcrystalline orientation, had not been clarified.

In the present paper, the low temperature carbonized PAN fibers with the seven-stage procedure were self-
made in the laboratory. The evolution mechanism of chemical structure and aggregation structure of the
cyclized structure of PAN precursor was investigated. The change characteristics of tension and orientation
structure during the low-temperature carbonization process were also studied by means of the methods, such as
TG, 13C-NMR, XRD, XPS and Raman, in order to achieve the efficient development orientation of carbon
crystallites. This was important for the controlling of the reconstruction of the cyclized structure in low-
temperature carbonization process, which was meaningful to the tension controlling in different stages of low-
temperature carbonization process for the formation of efficient oriented growth of carbon crystallites.

2. Materials and methods

2.1. Raw materials and sample preparation

In the present paper, the wet spinning process was applied to produce the PAN precursor fiber in laboratory. The
precursor structure was composed of the acrylonitrile copolymer and itaconic acid, and the content of itaconic
acid was less than 1%. Then the PAN precursor fibers were continuously heat-treated in the 6-stage pre-
oxidation furnaces. The temperatures from 1# to 6# pre-oxidation furnaces were set as 160, 200, 220, 240, 250
and 260 °C, respectively, and the total pre-oxidation time was about one hour.

The low temperature carbonization process of PAN pre-oxidized fiber was carried out in the carbonization
furnace under the protection of nitrogen atmosphere. The setting temperature of low-temperature
carbonization process was based on the thermal gravimetric behavior of PAN pre-oxidized fiber in nitrogen
atmosphere, as shown in figure 1.

As shown in figure 1, it could be observed that the weight loss rate reached the maximum when heat-treated
temperature was about 400 °C. It has been proved that there were large number of non-cyclized and non-
crosslinked groups in PAN fiber after the pre-oxidation process. During the carbonization process, the groups
would undergo the further chemical reaction and release the small molecular by-products, which significantly
affected the weight loss of the fiber [19–21]. Therefore, in this paper, the temperature setting range in low-
temperature carbonization was selected from 300 °C to 650 °C. The low temperature carbonization process of
each sample was as following:

The pre-oxidized fiber was first heat-treated at 300 °C in nitrogen atmosphere for 4 min, obtain the post-
treatment fiber. Then the post-treatment fibers were heat-treated in nitrogen atmosphere for carbonization at
350, 400, 450, 500, 550, 600 and 650 °C, respectively. During the process, the fiber length was kept constant, and
the heat-treated time at different temperatures was 4 min. The schematic of the low temperature carbonization
treatment device is shown in figure 2. The carbon fibers at different temperatures were collected and named LF-
350, LF-400, LF-450, LF-500, LF-550, LF-600 and LF-650, respectively.
2.2. TGA measurements
Thermogravimetric analysis (TGA) was conducted using a TA SDT-Q600 instrument. The pre-oxidized fiber was heated from 100 to 900 °C at a heating rate of 10 °C min⁻¹. The nitrogen gas was used at a constant flow of 100 ml min⁻¹. The sample mass for the measurement was approximately 5 mg.

2.3. 13C-NMR measurements
13C-NMR spectra of carbonized fiber were obtained through a Bruker AV-300 NMR spectrometer equipped with a 4 mm cross-polarization/magic-angle spinning (CP/MAS) probe with a rotation speed of 12 kHz. A resonance frequency was 73.5 MHz, the cumulative scanning times was 300–3000 s, and the single scanning time was 10 s. Tetramethylsilane (TMS) was used as the internal reference to determine the chemical shifts.

2.4. Raman analysis
The micro confocal Raman spectrometer (RM 2000) produced by Renishaw company (UK) was used with He-Ne laser. The wavelength of the incident light was 532 nm. The scanning range was 900–1900 cm⁻¹, and the laser power was controlled to be less than 0.5 mW to avoid heating the samples.

2.5. XRD measurements
X-ray diffraction (XRD) patterns of samples were recorded with an X’Pert PRO MPD diffractometer using Cu Kα radiation at 40 kV and 40 mA. The scanning angle range was 5° ~ 90° and the scanning step size was 0.02°. The XRD diffraction curve were fitted by the Lorentz–Gauss area function using PeakFit v4.12 software to acquire the parameters of peak position, peak intensity and full width at half maximum height (FWHM). The spacing ($d_{002}$) of pseudo-graphite crystallites was calculated according to Bragg equation, as following:

$$2d_{002} \sin \theta = \lambda$$

(1)

where $d_{002}$ is the spacing of (002) miller plane, $\lambda$ is the X-ray wavelength (0.154 nm); $\theta$ is the diffraction angle of (002) miller plane. The crystallite size was calculated according to Scherrer equation [22], as following:
\[ L(c) = \frac{K \lambda}{\beta \cos \theta} \]

where \( L(c) \) represents the crystallite size along (002) plane. \( \beta \) is the half-width of the 002 diffraction peak at \( 2 \theta \) (25.2°), \( K \) is a constant (0.94), \( \lambda \) is the X-ray wavelength (0.154 nm), and \( \theta \) is the Bragg angle of the (002) diffraction.

Azimuthal scans were carried out at \( 2 \theta \) (25.2°) in the range of 90° \( \sim \) 270°. The scanning step was 0.5°. The degree of orientation (\( f_c \)) was calculated by scanning the FWHM (\( H \)) of X-ray diffraction peak in azimuth [23], as following:

\[ f_c = \frac{180 - H}{180} \times 100\% \]

### 3. Results and discussion

#### 3.1. Evolution of cyclized structure of PAN stabilized fiber during the low temperature carbonization

\(^{13}\)C-NMR was used to characterize the changes of carbon atom state of PAN stabilized cyclized structure [24] as shown in figure 3. \(^{13}\)C chemical shifts and corresponding chemical groups were shown in table 1. It was shown that with the increase of heat-treated temperature, the position of \(-\text{C}═\text{C}\) resonance peak at 136 ppm gradually shifted to lower chemical shift, while the intensity of carbon resonance peak at 10–40 ppm decreased rapidly and almost disappeared above 450 °C. The relative content of other characteristic peak showed different variation tendency.

Figure 4 indicated that the change of the \(-\text{C}═\text{N}\) resonance peak moved towards the lower chemical shift direction with the increase of temperature. When the heat-treated temperature was lower than 450 °C, the chemical shift of \(-\text{C}═\text{C}\) group was relatively higher. When the temperature increased up to 550 °C, a wide peak formed in the range of 129.4 \( \sim \) 125.5 ppm (figure 3). According to reference [23], there was a linear relationship between NMR peak position and \( \pi \) electron cloud density with aromatic ring structure. With the increase of \( \pi \) electron cloud density, the chemical shift moved to the lower chemical shift direction. It was considered that the

\[ \text{Table 1. } ^{13}\text{C resonances observed in NMR spectra and the corresponding chemical structure.} \]

| Peak no. | \(^{13}\text{C chemical shift (ppm)}\) | Chemical group |
|---------|-----------------------------------|----------------|
| a       | ~30                               | \(-\text{CH/CH}_2\) |
| b       | 115                               | \(-\text{C}═\text{CH}\) |
| c       | 121                               | \(-\text{C}≡\text{N}\) |
| d       | 136                               | \(-\text{C}═\text{C}\) |
| e       | 153                               | \(-\text{C}═\text{N}\) |
displacement of $-\text{C}=\text{C}$ resonance peak revealed the development characteristics of aromatic ring structure in the stage of low temperature carbonization. Combined with the TGA curve of PAN pre-oxidized fiber in figure 1, it was indicated that the large number of pyrolysis reactions of small molecules or small ring structure occurred, which significantly affected the weight loss of the fiber. However, the structural size of aromatic heterocycles did not change significantly at this stage. It means that it had little effect on the change of $-\text{C}=\text{C}$ peak. When the heat-treated temperature was above 450 °C, the pyrolysis reaction was slowed down (figure 1). It was considered that the intermolecular polycondensation and reconstruction gradually increased during this stage. On the one hand, the slow pyrolysis reaction and polycondensation reaction affected the weight loss continuously. On the other hand, the polycondensation and recombination caused a significant increase in aromatic carbon structure and formed a larger carbon based planar structure, which affected the increasing of the displacement of $-\text{C}=\text{C}$ peak. Especially after heat-treated at 550 °C, the thermal weight loss rate quickly decreased to the lowest and tended to be flat (figure 1). It was concluded that at this stage, the pyrolysis reaction of a large number of small molecules was coming to finish, and the polycondensation and recombination reaction mainly occurred, resulting in the formation of larger carbon base planar structure. This affected the further increase of the displacement of $-\text{C}=\text{C}$ peak, and formed a broad peak at the lower chemical shift.

Furthermore, the $^{13}$C-NMR curve in figure 3 was fitted by peaks, and the peaks area of the characteristic peaks was normalized to obtain the relative content of chemical groups corresponding to each characteristic peak. Its variation tendency with the increase of heat-treated temperature was shown in figure 5. As shown, the relative contents of $-\text{CH}/\text{CH}_2$ and $-\equiv\text{N}$ groups decreased with the increased temperature. When the heat-treated temperature was above 450 °C, the $-\text{CH}/\text{CH}_2$ group basically disappeared and the $-\equiv\text{N}$ group basically disappeared after 500 °C. It revealed the pyrolysis characteristics of cyclized structure for PAN stabilized fiber in the initial stage of low temperature carbonization (mainly in the range of 350 to 450 °C). The $\text{C}=-\text{C}$ bond between $-\text{CH}/\text{CH}_2$ in the linear or partial cyclized structure of PAN molecular chains began to break at the low temperature carbonization stage. In addition, the acyclic $-\equiv\text{N}$ further reacted in this stage. Part of $-\equiv\text{N}$ groups formed into the double bond structure, and some $-\equiv\text{N}$ groups were combined with adjacent $-\text{H}$ and were removed in the form of HCN. It affected the decreasing of the relative content of $-\equiv\text{N}$, while the contents of $-\text{C}≡\text{N}$ and $-\text{C}≡\text{CH}$ increased.

$-\text{C}≡\text{N}$, $-\equiv\text{C}$ and $-\equiv\text{C}≡\text{H}$ were the groups that exist in the low-temperature carbonization process. With the increase of temperature, the relative content of $-\equiv\text{C}≡\text{H}$ group increased continuously, while $-\equiv\text{C}≡\text{H}$ and $-\equiv\text{C}≡\text{N}$ groups increased firstly and decreased gradually after 500 °C. These results indicated that the continuous dehydrogenation reaction and further reaction of $-\equiv\text{N}$ affected the continuous increasing of the contents of $-\equiv\text{C}≡\text{H}$, $-\equiv\text{C}$ and $-\equiv\text{C}≡\text{N}$ below 500 °C. Above 500 °C, the polycondensation and reconstruction of aromatic layer gradually appeared. A larger area of aromatic ring structure was generated, which affected the further rapid increase of $-\equiv\text{C}≡\text{H}$ content. At the same time, $-\equiv\text{C}≡\text{H}$ and $-\equiv\text{C}≡\text{N}$ groups were released by means of small molecules such as HCN in the polycondensation reaction, which affected the significant reduction of their relative content.

Based on the above analysis, the evolution mechanism of cyclized structure for PAN stabilized fiber during the low temperature carbonization was proposed as shown in figure 6. With the increasing of low carbonization temperature, the cyclized structure increased gradually. Especially over 450 °C, the structure of discontinuous
Figure 5. Change of relative content of –CH/CH₂, –C=O, –C=CH, –C≡N, –C=N with increasing temperature.

Figure 6. Evolution mechanisms of low temperature carbonization reactions.
polycyclic aromatic carbon was affected by polycondensation and reconstruction increased significantly. Furthermore, when the temperature was higher than 550 °C, the pseudo-graphite based ring structure with large size was gradually formed.

### 3.2. Evolution of graphitized structure of PAN fiber during low temperature carbonization

The pseudo-graphite structure of PAN stabilized fibers heat-treated at different low carbon temperatures was characterized by Raman spectroscopy as shown in figure 7(a). The D peak near 1360 cm$^{-1}$ was caused by stretching vibration of sp$^3$ hybrid carbon atoms at the edge of graphite sheet or defects, which mainly reflected the structural characteristics of disordered graphite in carbon fiber. The G peak near 1580 cm$^{-1}$ was caused by the stretching vibration of sp$^2$ hybrid carbon atoms among the aromatic ring structure, which reflected the ordered graphite layer structure in the carbon fiber. The graphitization degree of carbon fiber (R) was usually characterized by the relative ratio of D peak and G peak ($R = I_D/I_G$) [26]. The smaller the R value, the higher the graphitization degree.

For Raman spectra of carbon materials with imperfect structure, except for D and G peak, it also had shoulder peak A at about 1500 cm$^{-1}$, which reflected the amorphous C structure in the structure of carbon materials, and the shoulder peak I at about 1200 cm$^{-1}$, which was still inconclusive [27, 28]. The Raman spectra curve of PAN stabilized fibers heat-treated at different temperatures were fitted as shown in figure 7(b), and the variation of characteristic peak parameters with increasing temperature was shown in figures 8 and 9.

Figures 3–7 showed the change of D peak position of PAN fiber during the low-temperature carbonization. Similar to figure 4, the position of D peak also showed that there was almost no obvious change below 450 °C. Then it shifted rapidly to low Raman shifting when the temperature was above 450 °C. Raman spectra of aromatic compounds showed that the peak position of D peak was very sensitive to the size and shape of
aromatic ring. When the size of aromatic ring in the planar structure of aromatic ring increased, D peak moved
to low Raman shifting direction \cite{29,30}. Therefore, it meant that when the low carbonization temperature was
lower than 450 °C, the main structure in the fiber was relative small ring structure, which had little effect on the
position of D peak. When the carbonization temperature was higher than 450 °C, the polycondensation and
reconstruction of several aromatic heterocyclic structures gradually transferred to a larger aromatic ring
structure, which affected the continuous shift of the position of D peak to low Raman shifting direction.

Figure 9 shows the variation of FWHM of D and G peaks (FWHM$_D$ and FWHM$_G$) for PAN stabilized fiber
during low temperature carbonization. It could be observed that with the increase of temperature, the FWHM$_D$
increased slowly at first followed by rapid change after 450 °C and relative slow change after 550 °C. The
FWHM$_G$ decreased significantly at first, and then decreased slowly over 450 °C. It was considered that the
FWHM$_D$ was related to the defects and edge structure of aromatic heterocycles. When the carbonization
temperature was lower than 450 °C, the main structure in the fiber were small aromatic heterocycles generated
in pre-oxidation process. At this stage, the small molecule pyrolysis reaction had relatively little effect on the
defects of cyclized structure resulted in the slow increasing of the FWHM$_D$. When the temperature was higher
than 450 °C, the polycondensation and reconstruction of aromatic heterocyclic structure gradually played more
important role. Affected by the difference of the spatial position of the cyclized structure, the early stage of
aromatic heterocyclic reconstruction process was random and unevenly distributed, forming a series of carbon
ring structures with different scales. At this stage, the homogeneity of carbon ring structure was low and the
defects increased significantly, which affected the rapid increase of FWHM$_D$. When the temperature was higher
than 550 °C, the pseudo-graphite based ring structure with large size gradually formed, and polycondensation
and reconstruction was gradually slown down. It resulted in the increasing tendency of FWHM$_D$. The FWHM$_G$
peak was related to the ordered graphite structure of aromatic heterocyclic fiber. With the increase of heat-
treated temperature, the scale of aromatic heterocycles gradually increased, which led to the increasing of
ordered carbon rings structure. Therefore, the FWHM$_G$ gradually decreased.

The variation of graphitization degree value (R) of PAN stabilized fiber heat-treated at different low carbon
temperatures was shown in figure 10. With the increase of temperature, R value decreased slowly at first and then
tended to more rapid after 450 °C. It indicated that the pseudo-graphite structure in the fiber gradually formed
and increased.

### 3.3. Evolution of aggregation structure of stabilized PAN fibers during low temperature carbonization

The aggregation structure change of stabilized PAN fiber during low-temperature carbonization was
characterized by XRD, which was shown in figure 11. The diffraction peak near 2θ = 17° was caused by the
residual linear molecular chains in PAN fiber. With the increase of temperature, the intensity decreased
gradually and disappeared completely after 450 °C. The peak near 2c = 25° was generally considered to be the
diffraction peak of (002) miller plane for carbon fiber. It does not exist in the pre-oxidation stage. It was usually a
relatively low-intensity and broad peak at the low-temperature carbonization process and then gradually
evolved into a sharp crystalline peak in the process of high-temperature carbonization. It was suggested that in
the process of low temperature carbonization, the pseudo-graphite crystallites had not been formed, but the
ordered structure in the direction of (002) peak had been begun to appear.
Through the Scherrer formula, the diffraction peak near $2\theta = 25^\circ$ was calculated to obtain the crystallite size ($L_C$) and spacing ($d_{002}$) of the fiber. The result was shown in figure 12. With the increase of temperature, $d_{002}$ decreased obviously at first, then slowed down after 450 °C. While the crystallite size $L_C$ increased slowly at first, then rapidly after 450 °C, afterwards slowly after 550 °C.

In order to study the effect of various stage structures formed by pyrolysis and reorganization on the crystalline orientation of the fiber during the low temperature carbonization process, all the samples (LF-350, LF-400, LF-450, LF-500, LF-550, LF-600 and LF-650) were further treated at 650 °C to obtain the final PAN based low carbonized fibers. The orientation of crystallites at each stage was characterized by XRD azimuth scanning. The result was shown in figure 13. With the increase of temperature, the orientation of the fiber first increased and reached the maximum value at 450 °C, and then decreased slowly.

Considering that the orientation structure was affected by the internal tension of the fiber, the internal tension was measured for the fiber carbonized at different lower temperatures and then carbonized during 650 °C. The result was shown in figure 14. When the treated temperature was lower than 450 °C, the main pyrolysis reaction occurred. The more sufficient the pyrolysis reaction was, the more effective the polycondensation reaction was after the further heat-treatment at 650 °C. It resulted in a significant increase in the tension within the fiber. Therefore, the degree of orientation was significantly improved (figure 13). When the temperature increased higher than 450 °C, the polycondensation reaction increased gradually. With the increase of temperature, the scale of the remaining non-polycondensated aromatic ring decreased gradually with
Figure 12. Variation of $I_{101}$ and $d_{002}$ with the increasing temperature.

Figure 13. Variation of crystalline orientation with the carbonization temperature.

Figure 14. Variation of tension in low-temperature carbonized at 650 °C.
the developing of polycondensation, which led to the gradual decreasing of tension during the heat-treatment at 650 °C. The improving effect on the orientation degree of carbon crystallites was weakened, and the orientation degree of carbon crystallites was reduced.

Through the change of PAN fiber cyclized structure and aggregation structure during the low-carbonization process, the model for tracing the pyrolysis and reconstruction of PAN cyclized fiber was proposed as shown in figure 15. Figure 15(a) showed the structure model of PAN pre-oxidized fiber, which was composed of amorphous structure and residual crystalline structure of PAN molecular chains. In the initial stage of low-temperature carbonization (350 ~ 450 °C), the dehydrogenation and pyrolysis reactions mainly occurred in the fiber. The original order structure was destroyed and formed small scale aromatic heterocyclic structures as shown in figure 15(b). When the low carbonization temperature was higher than 450 °C, the polycondensation and reconstruction of aromatic heterocyclic structure were gradually in domain and formed the polycyclic aromatic carbon structures with different scales. Under the induction of internal stress, these polycyclic aromatic carbon structures were further accumulated parallel to the fiber axis and gradually to be closed. \( d_{002} \) decreased gradually and the crystallites size increased slightly. The basement of pseudo-graphite crystalline structure was gradually formed as indicated in figure 15(c). With the further increase of temperature, \( d_{002} \) decreased furthermore and \( L_c \) increased slowly. It led to a new order structure similar to final structure of carbon fiber was gradually developed.

4. Conclusions

Through the pyrolysis, polycondensation and reconstruction, the cyclized structure and its aggregation structure of PAN-based pre-oxidized fiber in the process of low-temperature carbonization were significantly changed.

At the first stage, when the heat-treated temperature was lower than 450 °C, the mainly chemical reactions were the dehydrogenation and pyrolysis in acyclic linear molecular chain or partial cyclized structure. At this stage, the growth of cyclized structure was not obvious. However, a large number of pyrolysis affected the destruction of the original pre-oxidized structure. It led to significant increase of internal stress and further induced the reorientation of the cyclized structure.
At the second stage, when the heat-treated was higher than 450 °C, the degree of dehydrogenation and pyrolysis decreased rapidly and the polycondensation and reconstruction of aromatic heterocyclic structure was gradually in domain. The early reconstruction process of aromatic heterocycles was random and unevenly distributed. A series of heterocycles structures with different scales was formed with defects and was further aligned under the induction of tension. At this stage, the new pseudo-graphite crystalline structure gradually formed, and the d-spacing of graphite layer decreased slightly and crystallites size increased slowly with the increase of heat-treated temperature.

At the third stage, after the heat-treatment at 550 °C, the pseudo-graphite base structure formed gradually. With the increase of heat-treated temperature, the d-spacing were further reduced slightly, and the crystallites size increased slowly. A new ordered structure similar to final structure of carbon fiber was gradually developed.

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Data availability statement

No new data were created or analysed in this study.

Author contributions

C.L., B.W. and S.W. conceived and designed the experiments; B.W. and S.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.

ORCID iDs

Chenggao Li  https://orcid.org/0000-0002-4338-8944

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