Effect of ambient atmosphere on the formation and evolution of conjugated structure of pre-oxidized polyacrylonitrile

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Abstract

The ambient atmosphere has the remarkable effect on the chemical reaction mechanism and the formation of characteristic chemical structures and conjugated structures for pre-oxidized polyacrylonitrile (PAN). In the present paper, fourier transform infrared spectroscopy (FT-IR) and ultraviolet visible spectroscopy (UV–vis) were used to characterize the variations of chemical reaction characteristic structures and conjugate structures of copolymerized PAN in nitrogen and air atmosphere, respectively. Combined with the multivariate reaction model proposed by the predecessors, it can be found that two main conjugated structures (conjugated polyene and conjugated aromatic heterocycle) formed during the pre-oxidation process of copolymerized PAN. In nitrogen atmosphere, the formed main structure units were the conjugated diene and conjugated double ring with 1–2 double bonds. By contrast, the formed main units in air were the conjugated diene and conjugated tricyclic with a double bond. During the whole pre-oxidation process, the maximum unit numbers of conjugated double bonds and conjugated rings were no more than four and six, respectively. Increasing the heat treatment temperature favored to form more conjugate structures than prolonging the heat treatment time. Furthermore, with the increase of heat treatment temperature or time in air, the main conjugate unit numbers had no obvious change, while the maximum unit numbers increased slightly. For the exposure in nitrogen atmosphere, the main conjugated polycyclic structure was transformed into conjugated tricyclic structure after the heat treatment at 250 °C for more than 3 h. In addition, when the heat treatment temperature and time were 280 °C for more than 4 h, the main conjugated polyene structure was transformed into conjugated triene, and the maximum conjugated unit numbers increased slightly.

1. Introduction

Polyacrylonitrile (PAN) based carbon fiber is an important reinforcement material to prepare the advanced fiber reinforced polymer composites and applied in different fields, such as aerospace, automation, rail transportation, marine structures and underground oil production engineering [1–3]. The excellent performance of carbon fiber largely depends on the pseudo graphite sheet structure generated during the graphitization process [4–6]. How to control the growth degree of pseudo graphite structure has become an important method to improve the mechanical and thermal properties of carbon fiber.
Some researchers proposed that the pseudo graphite sheets containing carbon ring and π-conjugate bond presented the carbon conjugate plane, which was gradually evolved from the conjugated aromatic ring structure formed during the pre-oxidation stage [7–9]. However, so far, there was still no in-depth study on the effects of environmental factors on the embryonic conjugate structure characteristics and its evolution mechanism during the pre-oxidation stage.

During the pre-oxidation stage of PAN, the transformation from linear molecular chain to trapezoidal ring structure is usually completed in air between 180 °C and 280 °C [10, 11]. In this period, the chemical reaction mechanism is complex, and the formed structures are diverse [12–16]. Meanwhile, the structural evolution was influenced by the factors, such as heat treatment environment, time-temperature effect and copolymer composition [17–20].

Related investigations have revealed the chemical reaction mechanism and product structure during the pre-oxidation process can be obtained by means of infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) and Raman spectra. Furthermore, the mechanisms of ‘cyclization reaction’, ‘dehydrogenation reaction’ and ‘oxidation reaction’ were proposed in the research [21–23], as well as the structural models of ‘trapezoidal structure’, ‘aromatic heterocycle’, ‘imine crosslinking’, ‘polyene amine’ and ‘spread crosslinking’ [24–26]. However, the effect mechanism of characteristic structure on the formation and evolution of embryonic conjugate structure has not been well established.

Relevant scholars have put forward that the characteristic structure formed during the pre-oxidation process included C=O, C=O and aromatic heterocyclic conjugated groups, which could be characterized and analyzed by UV–vis spectroscopy [27, 28]. This was because the absorption wavelength of UV–vis absorption spectrum was usually in the range of 200–800 nm, and it could significantly characterize the π–π* and π–π* orbital transitions of unsaturated bond conjugated systems. Kubasova et al [29] studied the UV–vis absorption spectrum of PAN/DMF dilute solution after the low heat treatment temperature at 153 °C, and they found that there was an obvious absorption peak with λmax about 350 nm. It was speculated that a conjugate system including 5–6 double bonds has formed. In fact, the pre-oxidation degree of PAN heat-treated at low-temperature was low, which mean PAN could not be completely dissolved after the full pre-oxidation treatment. Therefore, it was difficult to obtain the parameter changes of conjugated structure during the whole pre-oxidation process by using the solution method for the UV spectral characterization.

In the present paper, PAN film samples were designed and prepared. By adding a heating device to the spectrometers, FT-IR absorption spectra and in situ UV–vis spectra of PAN during the heat treatment in nitrogen and air atmosphere from 180 to 280 °C were obtained, respectively. The formation process of chemical reaction structure and conjugate structure of PAN during the whole heat treatment process were detected, which solved the capture problem of conjugated structure of PAN during the process of higher temperature pre-oxidation process. Furthermore, combined with the multivariate reaction model, the correlation between the characteristic chemical structure affected by the chemical reaction mechanism and the conjugated structure of PAN during the pre-oxidation process was established. Compared with the previous studies on the characterization of PAN conjugated structure in single atmosphere or regional heating temperature, the main structure form of PAN conjugated system in nitrogen and air atmospheres and its evolution mechanism with time and temperature were further put forward in the present paper. It would provide a theoretical basis for the regulation of conjugated structure of PAN during the pre-oxidized process.

2. Materials and methods

2.1. Raw materials and sample preparation

The white PAN copolymer powder containing less than a few percent of co-monomer (itaconic acid) was purchased from Jilin Chemical Fiber Company (Changchun, China) and it was prepared by free radical polymerization. PAN powder was firstly dissolved in dimethyl sulfoxide (DMSO) with the mass concentration ratio of 0.5 wt%, and then drop cast into glass trays. These trays were subsequently placed into a vacuum oven for vaporizing the solvent at 60 °C for 24 h. Finally, the PAN films were peeled off from the trays and washed by deionized water, and dried to obtain the constant weight. It was worth mentioning that the samples for in situ UV–vis test were prepared on a quartz substrate through the same solution casting method. Only several drops were used to ensure the thickness of the films.

2.2. UV–vis spectroscopy measurements

UV–vis spectroscopy measurements through the instrument of Shimadzu UV–2450 were carried out to study the evolution mechanism of conjugated structure with the slit width of 2 nm. The wavelength sweep range was from 200 to 800 nm with the medium sweep speed. A Linkam FTIR 600 hot platter with quartz windows was set into the light path of UV–vis spectrometer. The thin PAN film with its quartz substrate was quickly heated to...
180, 220, 250 and 280 °C at 100 °C min⁻¹ under the flow of nitrogen for 7 h. The spectra were collected after the different time scales (10, 30, 60, 120, 180, 240, 300, 360 and 420 min). Similarly, the parameter settings of UV–vis spectroscopy measurements in air were the same with the nitrogen atmosphere.

2.3. FT-IR spectroscopy measurements
FT-IR spectroscopy measurements through the instrument of Nicolet 5700 were carried out to study the evolution mechanism of chemical structure of PAN. The scanning scope was from 400 to 4000 cm⁻¹ with the resolution of 8 cm⁻¹. The same hot platter with ZnSe windows was also used to detect the changes of characteristic functional groups. The test conditions were same just as UV–vis measurements.

Relative cyclization rate (RCI) was calculated through the equation (1) \[ RCI = \frac{I_{C=O}}{I_{C=N} + I_{C=O}} \times 100\% \]

and relative content of other functional groups (Ra) under the same heat treatment conditions can be calculated by the equation (2) as following:

\[ R_a = \frac{I_a}{I_{C=N} + I_{C=O}} \times 100\% \]

where I_a denotes the relative intensity of a characteristic functional group, and its subscripts represent the characteristic functional groups (such as –C=C, –C≡O and –C≡N).

3. Results and discussion

3.1. Conjugated structures of pre-oxidized PAN at different ambient atmospheres
The chemical structures of PAN copolymer films formed during the pre-oxidation process in nitrogen and air atmosphere were different, which had the obvious effect on the formation and evolution of conjugated structures. Figure 1 shows the FT-IR spectra of pre-oxidized PAN film heat-treated at 250 °C for 1 h in nitrogen and air atmospheres of (a) in situ measurement of FT-IR spectra and (b) relative content of chemical characteristic functional groups of pre-oxidized PAN film.

Figure 1. The in situ measurement of FT-IR spectra of pre-oxidized PAN film heat-treated at 250 °C for 1 h in nitrogen and air atmospheres of (a) in situ measurement of FT-IR spectra and (b) relative content of chemical characteristic functional groups of pre-oxidized PAN film.
Figure 2. In situ UV–vis spectra of pre-oxidized PAN film heat-treated in nitrogen and air atmospheres at 250 °C for 1 h.

The relative contents of several characteristic functional groups generated after the pre-oxidation in nitrogen and air atmosphere were shown in figure 1(b). It can be found that the relative contents of C=–N groups (1620 cm⁻¹) were almost the same in nitrogen and air atmospheres. While the relative contents of C=–C (1580 cm⁻¹) and C=–O (1670 cm⁻¹) groups in air atmosphere were relatively larger than that of in nitrogen.

The characteristics conjugated structures formed in nitrogen and air atmospheres were characterized by UV–vis spectrum, as shown in figure 2. From the in situ UV–vis spectra, it can be found that PAN copolymer film without the pre-oxidation treatment had an absorption peak at about 200 nm, which was considered to be caused by the residual solvent (DMSO) in the film [32]. The residual solvent would be decomposed and removed after the heat treatment, which had no obvious effect on the pre-oxidation structure of PAN. In addition, figure 2 showed that there were two obvious absorption peaks whether in nitrogen or in air. The maximum absorption wavelength of the above two peaks heat-treated in nitrogen appeared at about 250 nm and 360 nm, respectively. In comparison, these peaks heat-treated in air were wider. Especially, the second peak heat-treated in air had an obvious red shift, which indicated that the conjugated structure of PAN pre-oxidized in air increased significantly.

Relevant research showed that the significant absorption peak of UV–vis spectrum near 250 nm appeared, which was a double bond conjugate structure in the molecule [33]. Furthermore, the absorption peak near 300–400 nm for pre-oxidized PAN was related to the conjugated structure of aromatic heterocycles [33]. Figure 3 shows the absorption peak (λ_max) of π–π* transition for the reference material with linear polyene and fused ring structure, and its relationship with the number of double bonds and rings. Through the linear fitting method, the relation between the double bond number and λ_max was found to approximately follow the logarithmic law. Furthermore, the relation between the fused ring number and λ_max followed the linear law. Based on figure 2, it was roughly inferred that the first absorption peak (about 200–300 nm) of the UV–vis spectrum for pre-oxidized PAN was mainly the carbon–carbon double bond conjugate structure (C=–C) with 2–5 basic units. The second absorption peak (about 300–600 nm) was mainly the aromatic heterocyclic conjugate structure with 2–5 basic units.

Further analysis was conducted on the relationship between the measured value of λ_max (figure 2) and theoretical value of λ_max (figure 3). For the first absorption peak, compared with the conjugated diene λ_max about 217 nm, the measured λ_max was about 250 nm and had a difference of 33 nm. Considering the effect of double bond alkyl substitution and trans stereostructure on the red shift of UV absorption band, it could be inferred that the conjugate structure represented by the first absorption peak (about 200–300 nm) was mainly the conjugated diene structure and a small part was conjugated triene structure. In air atmosphere, the participation of oxygen promoted the dehydrogenation reaction, which caused the increase of C=C conjugate structure content. Meanwhile, the relative broadening of the first absorption peak changed with it. The conjugated structure can be named after the number of continuous C=C as shown in figure 4. As shown, it mainly included (n_{b,2}) and (n_{b,3}) conjugation.

For the second absorption peak heat-treated in nitrogen, λ_max at about 360 nm was higher than that of naphthalene (λ_max at about 275 nm) with a difference of 85 nm, and was lower than that of diazepine (λ_max at
about 308 nm) with a difference of 52 nm. The effects of the dehydrogenation N atoms in the ring could be ignored. Considering adding a conjugate double bond out of the ring, \( \lambda \) could increase by about 30 nm. It can be speculated that the main unit of conjugate structure was a bicyclic conjugate structure and contained at least one outer double bond. When PAN was heat-treated at 250 °C in nitrogen atmosphere for 1 h, \( \lambda_{\text{long}} \) extended to about 565 nm. It can be speculated that the number of basic units of fused rings structure should not exceed four.

For the second absorption peak heat-treated in air, \( \lambda_{\text{max}} \) located at about 395 nm. It was speculated that the main structure was the 3-ring conjugate structure. In addition, the C=O and –OH substituted the ring structure owing to the participation of oxygen and had the effect on a small amount of red shift of absorption peak. \( \lambda_{\text{long}} \) extended to about 720 nm when the heat-treated temperature was 250 °C. It can be speculated that the basic unit number of fused rings should not exceed five. These above conjugated structures could be named after the number of conjugated rings (\( m_r \)) and double bonds outside the ring (\( n_{cb} \)) in figure 5, as following:

### 3.2. Evolution mechanism of conjugated structure of pre-oxidized PAN in nitrogen and air atmospheres

PAN copolymer films were heat treated in nitrogen and air at 250 °C for different time to study the variations of UV–vis spectra, which further revealed the evolution mechanism of conjugated structure formed during the PAN pre-oxidation process. As shown in figure 6, the absorption peaks with \( \lambda_{\text{max}} \) at about 250 nm and 360 nm began to appear after the heat treatment at 180 °C in nitrogen for 10 min. This indicated that in the initial stage of pre-oxidation reaction, the diene conjugation and bicyclic conjugation structures appeared. With the extension of heat treatment time, the intensity of the above two absorption peaks increased rapidly at first and tended to be slow. The second absorption peak gradually red shifted and widened, and after the heatment of seven hours, \( \lambda_{\text{max}} \) red shifted to 396 nm.

In air atmosphere, after the heat treatment at 180 °C for 10 min, the absorption peaks with \( \lambda_{\text{max}} \) at about 250 nm and 395 nm became to be obvious. It indicated that diene conjugation and 3-ring conjugation structures...
were easier to form in a short time compared to the nitrogen atmosphere. With the extension of time, the intensity of the two absorption peaks firstly increased rapidly, and then increased slowly. The first absorption peak red shifted slightly and the second absorption peak widened gradually. The variations of $\lambda_{\text{max}}$ and $\lambda_{\text{long}}$ of the above two absorption peaks were affected by heat treatment time and shown in figure 7.

Combined with in situ FT-IR spectroscopy, the changes of chemical structure of PAN with the heat treatment time in nitrogen and air atmosphere at 250 $^\circ$C were characterized. It could reveal the evolution mechanism of conjugated structure. As shown in figure 8, with the extension of time, the relative cyclization rate ($R_{\text{Cl}}$) and the relative content of C= C ($R_{\text{C} = \text{C}}$) firstly increased rapidly, then slowed down after the heatment of 1 h, which was consistent with the variations of $\lambda_{\text{max}}$ (figure 7) and $\lambda_{\text{long}}$ (figure 6).

In addition, figure 8(a) showed that $R_{\text{Cl}}$ in air was significantly higher than that of in nitrogen before the heat treatment for 1 h. However, the difference of $R_{\text{Cl}}$ decreased gradually with the heat-treated time. When the heat-treated time was more than 1 h, $R_{\text{Cl}}$ in air was similar to that of in nitrogen. Corresponding to figure 7(b), $\lambda_{\text{max}}$ of the second absorption peak in air remained unchanged, while it red shifted in nitrogen after 4 h. It was speculated that the main conjugate structure (3-ring conjugate structure) in air kept unchanged with time. However, it changed from 2-ring conjugation to 3-ring conjugation in nitrogen, which caused $\lambda_{\text{max}}$ in nitrogen gradually growing to be similar to in air after 7 h.

Figure 8(b) showed that $R_{\text{C} = \text{C}}$ in air was relatively larger than that of in nitrogen. It was consistent with the previous research that ambient oxygen could promote the dehydrogenation reaction [22]. It was further revealed that under the same time and temperature conditions, the polyene conjugated structure generated in air was relatively more than that of in nitrogen, which caused the first absorption peak relatively broader (figure 6). Furthermore, it was considered that with the $R_{\text{C} = \text{C}}$ increased, the first absorption peak in air appeared red shifted after 2 h (figure 7(a)). It was speculated that the main conjugated polyene structure in air changed from conjugated diene to conjugated triene with the heat-treated time.
3.3. Effect of time-temperature effect on the evolution of conjugated structure of pre-oxidized PAN

The effects of time and temperature on the evolution of conjugated structure of pre-oxidized PAN were investigated. Figure 9 shows the variation of the relative intensity of UV–vis absorption peaks heat-treated in nitrogen and air by the time-temperature effect.

The relative intensity of UV–vis absorption peak ($RI$) was calculated as shown in equation (5). Here $A_t$ is the absorption peak intensity at each constant temperature-time point, and $A_{7t}$ represents the absorption peak intensity at the corresponding constant temperature for 7 h.

$$RI = \frac{A_t}{A_{7t}} \times 100\%$$

Figure 9 took the treatment in nitrogen as an example. It could be seen that the conjugate structure increased almost linearly at 180 °C for 7 h. While for the temperature of 220 °C–250 °C, the growth of the two conjugated structures could be divided into three stages. Among them, it increased rapidly for 1 h ago, then slowed down, and finally further slowed. There was still a stable stage at 280 °C, and the intensity of the absorption peak hardly changed. Moreover, the growth rate of both conjugated structures increased significantly with the increase of temperature. When entering the slow growth stage, the higher the temperature, the earlier the time to enter this stage. The results showed that during the pre-oxidized process, high temperature promoted the movement of molecular segments, which was conducive to the rapid formation of a certain amount of conjugated structures in a short time.
The change rates of relative intensity of UV–vis absorption peak with the time at different heat treatment temperatures and atmospheres were linearly fitted in the first stages. The relevant parameters were listed in tables 1 and 2. It can be found that the relative content and growth rate of conjugated polyenes in air were larger than that of in nitrogen. It was revealed that it was easier to promote the rapid formation of polyene conjugated structure in air. Furthermore, when the temperature was below 220 °C, the relative content and growth rate of conjugated polycyclic structure in air were slightly higher than that of in nitrogen. While over 250 °C, the relative content and growth rate in air was close to that in nitrogen. This is consistent with the promotion effect of ambient oxygen on cyclization reaction in the early stage of pre-oxidation reaction.

The effects of time and temperature on the evolution of the conjugate structure unit for pre-oxidized PAN were investigated. As shown in figure 10, the variations of \( \lambda_{\text{max}} \) and \( \lambda_{\text{long}} \) of the two UV–vis absorption peaks in different atmosphere with the time and temperature were obtained, respectively. It could been seen that, below 250 °C, \( \lambda_{\text{max}} \) of pre-oxidized PAN remained unchanged with the time, indicating that the main conjugated structure unit was unchanged. When the temperature was above 250 °C, it was easier to promote the further red
shift of the two absorption peaks, this was $\lambda_{\text{max}}$ of the first absorption peak was about 263 nm, that of second absorption peak was about 400 nm. It was speculated that the main conjugated polycyclic structure in nitrogen gradually changed to conjugated tricyclic structure after the heat treatment at 250 °C for 7 h, and the main conjugated polyene structure changed to conjugated triene structure after the heat treatment at 280 °C for more than 4 h. While in air, there was no obvious change of the conjugate structural unit of the main body. This was consistent with the spatial configuration characteristics of random PAN molecular chain. On the same molecular chain, the number of adjacent cyano cyclization structural units would not be too many. $\lambda_{\text{long}}$ with heat treatment time and temperature showed that the maximum number of conjugate rings was no more than

![Figure 10. Evolution of $\lambda_{\text{max}}$ and $\lambda_{\text{long}}$ of conjugate structures for PAN film during pre-oxidation treatment in nitrogen and air with the time and temperature.](image-url)
six, which reflected the conjugated structure characteristics of adjacent molecular segments has crosslinked into rings.

Based on the above results, the evolution mechanism diagram of conjugated structure of pre-oxidized PAN in nitrogen and air atmospheres was shown in figure 11. The pre-oxidation process of copolymerized PAN mainly formed two conjugated structures: conjugated polyene and conjugated aromatic heterocycle. In nitrogen, the main units were the conjugated diene and conjugated double ring with 1–2 double bonds. While in air, the main units were the conjugated diene and conjugated tricyclic with a double bond. During the whole pre-oxidation process, the maximum unit number of conjugated double bonds was no more than four and that of conjugated rings was no more than six. In the initial stage of pre-oxidation at 180 °C, the main unit of conjugated structure had begun to form. By increasing the heat treatment temperature or prolonging the heat treatment time, it can promote the growth of conjugated structure to a certain extent.

4. Conclusions

The pre-oxidation process of copolymerized PAN mainly formed two conjugated structures: conjugated polyene and conjugated aromatic heterocycle. In nitrogen, the main units were the conjugated diene and conjugated double ring with 1–2 double bonds. While in air, the main units were the conjugated diene and conjugated tricyclic with a double bond. During the whole pre-oxidation process, the maximum unit number of conjugated double bonds was no more than four and that of conjugated rings was no more than six. This was consistent with the spatial configuration of random PAN molecular chain.

Due to the influence of ambient oxygen on the pre-oxidation reaction and formation structure, the content of conjugated polyenes of pre-oxidized PAN in air was relatively more than that of in nitrogen. While the content of conjugated aromatic heterocycles in air was slightly higher before 220 °C and close to that in nitrogen after 250 °C.

In the initial stage of pre-oxidation at 180 °C, the main unit of conjugated structure had begun to form. Further increase of the heat treatment temperature was easier to promote the rapid increase of conjugate structure than prolonging the time. In air, with the increase of heat treatment temperature or time, the main conjugate unit numbers had no obvious change, while the maximum unit numbers increased slightly. In nitrogen, after the heat treatment at 250 °C for more than 3 h, the main conjugated polycyclic structure was transformed into conjugated tricyclic structure. After 280 °C for more than 4 h, the main conjugated polycyclic structure was transformed into conjugated triene. The maximum conjugated unit numbers increased slightly.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

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

Conflicts of interest

The authors declare no conflict of interest.

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