Journal of Research in Science and Engineering (JRSE)
ISSN: 1656-1996 Volume-8, Issue-7, July 2026
DOI: 10.66069/ojspub.16560712

Kinetic Study on the Pre-oxidation Process of Polyacrylonitrile (PAN) Based on In-situ Infrared Spectroscopy

Jingjing Yan

College of Chemistry and Materials Science, Qinghai Minzu University, Xining 810007, China

Abstract: ***This study focuses on PAN films to investigate the kinetic characteristics and infrared spectral evolution during isothermal heat treatment under nitrogen and air atmospheres. Building upon conventional models, a two-parameter kinetic model consistent with experimental data under isothermal and equal-time conditions was developed to elucidate the dual role of oxygen in the reaction. The results indicate that, compared with the nitrogen atmosphere, the optimal temperature in air shifts downward by approximately 10°C, suggesting that the presence of oxygen lowers the optimal reaction temperature and enables higher reaction efficiency at relatively lower temperatures. The apparent rate constant initially increases and then decreases with rising temperature, further corroborating the dual-action mechanism of oxygen. In both atmospheres, the apparent equilibrium concentration decreases with increasing temperature; however, the values of the apparent equilibrium concentration (y_∞) in air are consistently higher than those in nitrogen at each temperature. Specifically, as the temperature increases, y_∞ declines by 15% in air, whereas it drops by 42% in nitrogen, implying that oxygen may shift the reaction equilibrium toward a higher residual cyano content, thereby hindering the cyclization reaction from achieving deep conversion. Moreover, the apparent activation energy and pre-exponential factor in air are both higher than those in nitrogen, reflecting that oxygen increases the complexity of the reaction pathways and the frequency of effective molecular collisions. This work provides a quantitative kinetic basis for understanding the regulatory role of oxygen in PAN pre-oxidation and for optimizing the stepwise temperature-rising process.***

Keywords: Polyacrylonitrile (PAN), Pre-oxidation, In-situ infrared spectroscopy, Kinetic model, Dual role of oxygen.

1. Introduction

Carbon fibers are widely utilized in aerospace, automotive energy, wind power, sports goods, and biomedical applications owing to their outstanding properties, including high strength, high modulus, light weight, high temperature resistance, and corrosion resistance [1-4]. Pre-oxidation, as a critical step in the manufacturing of carbon fibers, involves a complex interplay of chemical reactions and heat-and-mass transfer processes. The structure and performance of the pre-oxidized fibers result from the synergistic effects of multiple processing parameters, such as temperature, time, tension, and atmosphere [5,6]. These parameters not only independently influence the reaction rate and conversion degree but also jointly determine the radial chemical structure distribution and physical morphology evolution of the fibers through intricate coupling mechanisms [7]. Conventional infrared spectroscopy requires ex-situ sampling at different stages of the reaction, which makes it difficult to capture transient structural changes and dynamic information during the process. In recent years, the development of in-situ Fourier-transform infrared (FTIR) spectroscopy has overcome this limitation. By employing a specialized sample cell, an FTIR spectrometer can continuously acquire spectral data in real time under simulated reaction conditions with controlled temperature, atmosphere, and photo-irradiation [8]. In-situ FTIR enables the elucidation of true reaction pathways and the evolution of intermediate species, thereby offering new insights into theTo achieve precise control over the pre-oxidation process, kinetic studies are indispensable for quantifying reaction rates and revealing the energy barriers of different reactions [9,10]. The core of kinetic analysis lies in determining the three kinetic factors, namely, activation energy, pre-exponential factor, and reaction mechanism function [11]. The combination of quantitative analysis of infrared spectral peak areas with kinetic modeling constitutes a powerful paradigm for investigating polymer reaction processes. Traditional kinetic methods typically rely on data obtained from differential scanning calorimetry (DSC), thermogravimetry (TG), or X-ray diffraction (XRD) [12]. The commonly used kinetic approaches include model-fitting methods and model-free isoconversional methods. Model-fitting methods require a priori assumption of a reaction mechanism function, followed by fitting the experimental data to the model equation to extract kinetic parameters. The Kissinger method is a differential approach that utilizes DSC data at various heating rates for kinetic analysis. For instance, Xu Zhixian employed XRD analysis combined with a first-order kinetic equation to calculate an activation energy of 114.89 kJ/mol for the cyclization reaction in PAN pre-oxidation [13]. Zhao Genxiang defined an “aromatization index” (AI) and, through full-spectrum line-shape analysis of temperature-dependent spectra, obtained an activation energy of 95.6 kJ/mol for the cyclization reaction based on the Arrhenius theory [14]. Through such kinetic analyses, researchers have accumulated a wealth of activation energy data for the major reactions during PAN pre-oxidation. However, reported values vary considerably owing to differences in precursor composition, test conditions, and calculation methods [15]. In an inert atmosphere, because only cyclization and dehydrogenation reactions occur, the exothermic peak on the DSC curve is generally attributed to the cyclization reaction. The reported activation energies for cyclization span a wide range, roughly between 95 and 190 kJ/mol. Some studies using DSC and the Kissinger method have yielded values of approximately 120-160 kJ/mol, while XRD-based analyses have given values in the range of 95-115 kJ/mol [16]. Such discrepancies may originate from the type and content of comonomers, as cyclization initiated by an ionic mechanism typically exhibits a lower activation energy [17]. At present, kinetic research on

PAN pre-oxidation is rapidly advancing toward computational, multi-technique, and artificial-intelligence- based approaches [18]. Multi-scale methods, computational simulations, and the construction and decoupling of complex reaction equations are also current research hotspots. Researchers are no longer confined to single macroscopic thermal-analysis data; instead, they tend to combine macroscopic kinetic calculations with microscopic structural characterization (e.g., in-situ FTIR and in-situ XRD). By tracking in real time the changes in chemical groups and crystalline structures, a more accurate definition of reaction conversion can be achieved, leading to more reliable kinetic parameters. reaction mechanism.

In this context, the present work employs homogeneous PAN films as the research subject and utilizes in-situ FTIR spectroscopy to monitor the pre-oxidation behavior under various temperatures and atmospheres in real time. Meanwhile, based on conventional pre-oxidation kinetic models and taking into account the finite duration of isothermal treatment, we have developed a two-parameter kinetic model suitable for the pre-oxidation process of the PAN films used in this study. Nonlinear fitting of the experimental data is performed using MATLAB software to extract the kinetic parameters. This study systematically reveals the structural evolution and kinetic characteristics of the cyclization reaction under nitrogen and air atmospheres.

2. Experimental Section

2.1 PAN Raw Material

The raw material used in this study was laboratory-prepared polyacrylonitrile (PAN) powder, primarily composed of acrylonitrile (AN) and itaconic acid (IA). N,N-Dimethylacetamide (DMAC) was employed as the solvent. The detailed parameters of the PAN powder are summarized in Table 1.

Table 1: Detailed parameters of PAN powder

Monomer composition	Comonomer	Molecular weight (Mw)	Glass transition temperature (Tg)	Appearance	Solubility
Acrylonitrile (AN) ≥93%	Itaconic acid (IA) ~4%-6%	~80,000-100,000	~95-105 ℃	White powder	Soluble in polar solvents such as DMAC, DMF, and DMSO

2.2 Sample Preparation

The homogeneous PAN films used in the experiments were prepared by the solution casting method. First, 0.4808 g of PAN powder and 59.5204 g of DMAC solvent were placed into an 80 mL reagent bottle and stirred magnetically in a 65 ℃ water bath for 4 h to obtain a transparent PAN/DMAC solution with a mass fraction of 0.8 wt %. Then, 30 g of this solution was dropped onto a square glass plate pre-conditioned at room temperature and evenly spread. The plate was placed in a constant-temperature oven at 65 ℃ for 24 h to allow solvent evaporation, yielding a PAN film of uniform thickness. The film was peeled off and immersed in anhydrous ethanol, followed by extraction at 55℃ in a water bath for 1 h to remove residual solvent. After cooling to room temperature, the ethanol was decanted, and the film was dried in an oven at 65 ℃ until the ethanol had completely evaporated. Finally, the film was cut into discs with a diameter of 14 mm using a circular punching die for subsequent FTIR measurements.

2.3 Experimental Procedure

The isothermal pre-oxidation treatment of the prepared PAN films was carried out using a Nicolet iS50 Fourier-transform infrared spectrometer. Prior to the measurements, the instrumental parameters were set as follows: resolution of 2 cm^{-1}, spectral range of 4000-400 cm^{-1}, and 16 scans per spectrum. The experiments were conducted under both nitrogen and air atmospheres, and infrared spectra were sequentially collected at isothermal temperatures of 230 ℃, 240 ℃, 250 ℃, 260 ℃, and 270 ℃, so as to systematically investigate the effects of atmosphere and temperature on the kinetic parameters of the PAN pre-oxidation process.

2.4 Data Processing

The acquired infrared spectral data were pre-processed using 2DIR Professional I 001 software. The pre-processing procedure consisted of baseline correction followed by smoothing. Baseline correction was performed using a six-point correction method, with the correction center points set at 3600 cm^{-1}, 2300 cm^{-1}, 1900 cm^{-1}, and 850.00 cm^{-1}. Smoothing was carried out using a quadratic-cubic algorithm with a smoothing point number of 15.

The absorbance of the characteristic peak in the range of 2300-2100 cm^{-1} as a function of time was recorded using OMNIC software, and the time-dependent absorbance curves were plotted using Origin 2024 software.

The two-parameter kinetic model was fitted to the experimental data using the lsqcurvefit function in MATLAB R2024a. The apparent reaction rate constant (k), apparent equilibrium concentration (y_∞), and the sum of squared residuals (SSR) were output to evaluate the fitting quality. Based on the fitting results, the kinetic evolution during the pre-oxidation of PAN films was analyzed.

3. Construction and Solution of the Two-parameter Kinetic Model for PAN Pre-oxidation

3.1 Experimental Basis for Model Establishment

Isothermal heat treatment of PAN films was conducted under a nitrogen atmosphere, and the absorbance change of the characteristic nitrile (C≡N) peak at 2240 cm^{-1} was monitored via in-situ infrared spectroscopy. The dimensionless concentration of nitrile groups, denoted as y_{CN}, was obtained by normalization according to the Beer-Lambert law. Figure 1 presents the evolution curves of y_{CN} with time at different temperatures under nitrogen.

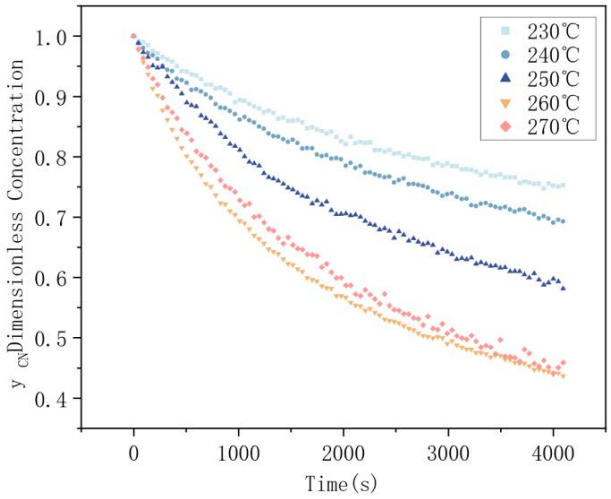

Figure 1: Evolution of the dimensionless nitrile concentration (y_{CN}) with time at various temperatures under nitrogen atmosphere

The experimental data reveal that within the finite isothermal treatment period of 4094 s, the final apparent residual nitrile concentration does not decay to zero at any of the temperatures examined. At 230 ℃, the apparent residual concentration is approximately 0.69, whereas at 270 ℃, it decreases to about 0.40. Higher temperatures correspond to lower apparent residual nitrile concentrations. This observation indicates that the cyclization reaction of PAN undergoes limited conversion under specific temperature, atmosphere, and time conditions.

3.2 Model Assumptions

Based on the experimental data presented in Figure 1, the following fundamental assumptions are proposed:

1) Under isothermal conditions within a finite time frame, the restricted nature of the cyclization reaction during PAN pre-oxidation can be characterized by the apparent residual nitrile concentration, y_∞, which is temperature-dependent.

2) The rate of the cyclization reaction is assumed to be proportional to the extent to which the current concentration deviates from the apparent residual nitrile concentration, with the driving force expressed as (y_{CN} - y_∞).

3) The cyclization reaction follows apparent first-order kinetics, behaving as an apparent first-order process, with the proportionality coefficient defined as the apparent rate constant k (with units of s^{-1}).

These assumptions condense the complex reaction mechanism into a model that aligns with the actual experimental observations and effectively captures the essential nature of the residual nitrile concentration during the later stages of the cyclization reaction.

3.3 Establishment and Solution of the Differential Equation

The experiments reveal that in the later stages of isothermal treatment, due to the finite reaction time, the nitrile concentration does not decay to zero as predicted by ideal kinetic models, but rather retains a certain residual value. Accordingly, based on conventional kinetic models, a two-parameter kinetic model adapted to the present experimental process is constructed as follows:

$$\frac{dy_{CN}}{dt} = k(y_{CN} - y_\infty) \quad (1)$$

where k is the apparent rate constant, whose magnitude reflects the overall rate of the cyclization reaction and embodies the kinetic characteristics of the process. The parameter y_∞ denotes the apparent residual nitrile concentration over a given period, which characterizes the extent of the cyclization reaction and is governed jointly by reaction thermodynamics and temperature, satisfying $0 < y_\infty < 1$. A smaller value of y_∞ indicates a more thorough cyclization reaction, whereas a larger value implies a higher proportion of unreacted nitrile groups, suggesting more pronounced restrictions arising from steric hindrance and molecular chain rigidity.

The negative sign in the equation signifies the decreasing trend of nitrile concentration with reaction progression, which is consistent with the experimentally observed decline in nitrile concentration over time.

The initial condition is set as $y_0 = 1$ at $t = 0$, which is in accordance with the experimental fact that the nitrile characteristic peak intensity is at its maximum at time zero and the relative concentration is unity. This initial condition ensures the linkage between the model and the experimental data.

Nonlinear fitting of the constructed kinetic model to the experimental data was performed using the lsqcurvefit function in the Optimization Toolbox of MATLAB R2024a.

4. Results and Discussion

4.1 In-situ FTIR Analysis of the Nitrile Characteristic Peak

1) Evolution of the nitrile characteristic peak under nitrogen atmosphere

Under nitrogen atmosphere, during isothermal treatment of PAN films in the temperature range of 230 ℃-270 ℃, the intensity and shape of the nitrile characteristic peak at approximately 2230-2240 cm^{-1} exhibit significant changes with temperature and time, reflecting the cyclization and crosslinking behavior of nitrile groups during the thermal stabilization process.

As shown in Figure 2, the nitrile peak intensity decreases monotonically with increasing heat-treatment time at all temperatures, but the decay rate and the final residual intensity vary with temperature. At 230 ℃, the nitrile peak intensity declines slowly over time, while the peak shape remains sharp and symmetric with no obvious new bands emerging. This indicates that the cyclization reaction at this temperature proceeds predominantly via intramolecular ring formation, with only a small fraction of nitrile groups participating in cyclization; the linear molecular chain structure remains dominant, and the degree of cyclization is relatively low. In the range of 240 ℃-250 ℃, as the temperature rises, the

molecular chains acquire sufficient energy, the cyclization rate increases, and the decay of peak intensity accelerates. When the temperature is elevated to 260 ℃, the decrease in peak intensity becomes more pronounced, indicating that the cyclization rate gradually accelerates with increasing temperature, and a large number of nitrile groups form conjugated C＝N bonds through cyclization, leading to a continuous reduction in the number of linear nitrile groups. At 270 ℃, the nitrile peak intensity drops sharply, suggesting that the reaction rate enters a phase of explosive growth.

With increasing pre-oxidation temperature, a new weak absorption shoulder appears at approximately 2200-2220 cm^{-1}. This shoulder corresponds to conjugated C＝N or cumulative double-bond structures formed during the cyclization process, marking the onset of the autocatalytic stage of the cyclization reaction. The conjugated ladder structures generated in the earlier stage enhance the reactivity of the remaining nitrile groups through strong electron-withdrawing effects or local ordered arrangements. This catalytic promotion accelerates the crosslinking and aromatization reactions involving nitrile groups, resulting in substantial consumption of the nitrile characteristic peak.

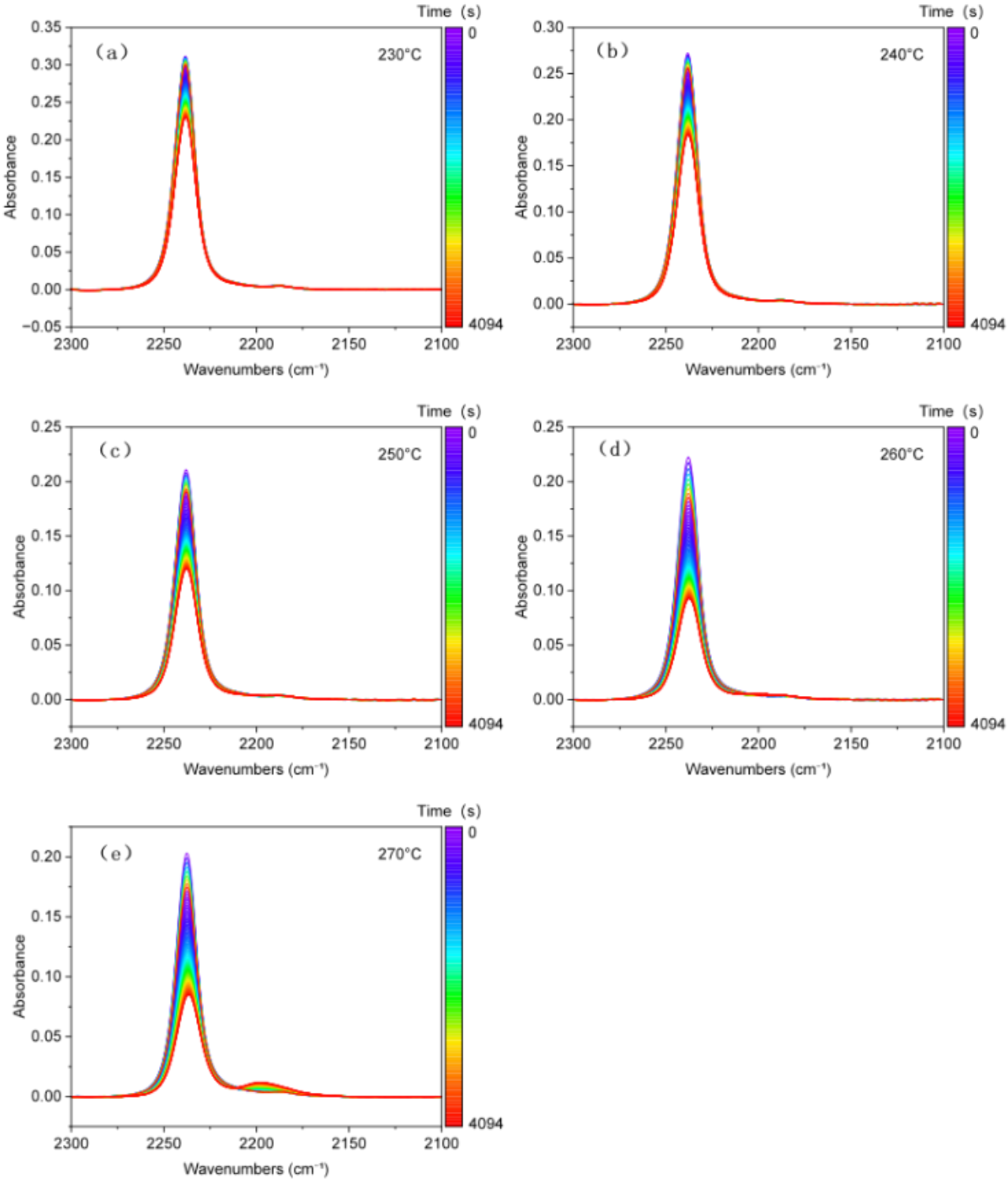

Figure 2: In-situ FTIR spectra of the nitrile characteristic peak region of PAN films during heat treatment at 230-270 °C under nitrogen atmosphere

2) Evolution of the nitrile characteristic peak under air atmosphere

Analysis of Figure 3 reveals that, at all temperatures, the main nitrile characteristic peak consistently appears at approximately 2245-2250 cm^{-1}, and its intensity decreases with increasing temperature. At 230 ℃, the absorbance of the main nitrile peak exhibits only minor changes over time. In the range of 240-250 ℃, the absorbance of the main nitrile peak begins to decline slowly with prolonged treatment time. At 260-270 ℃, the decreasing trend of the main nitrile peak becomes more pronounced over time, indicating an accelerated consumption rate of nitrile groups at elevated temperatures.

On the lower-wavenumber side of the main nitrile peak, at approximately 2200-2220 cm^{-1}, a new shoulder peak gradually emerges and intensifies with increasing temperature and extended treatment time. At 230-240 ℃, this region shows only a weak shoulder with no noticeable absorbance change. At 250 ℃, the shoulder becomes clearly distinguishable, and its absorbance progressively increases with time. At 260-270 ℃, the shoulder becomes more prominent, evolving into a secondary peak separated from the main nitrile peak, and its absorbance continues to rise over time, indicating the sustained formation of the corresponding chemical species at high temperatures. This shoulder peak is generally attributed to intermediate products of the cyclization/crosslinking reactions of nitrile groups, and serves as a typical marker for the cyclization and oligomerization reactions of nitrile groups during the thermal stabilization of PAN.

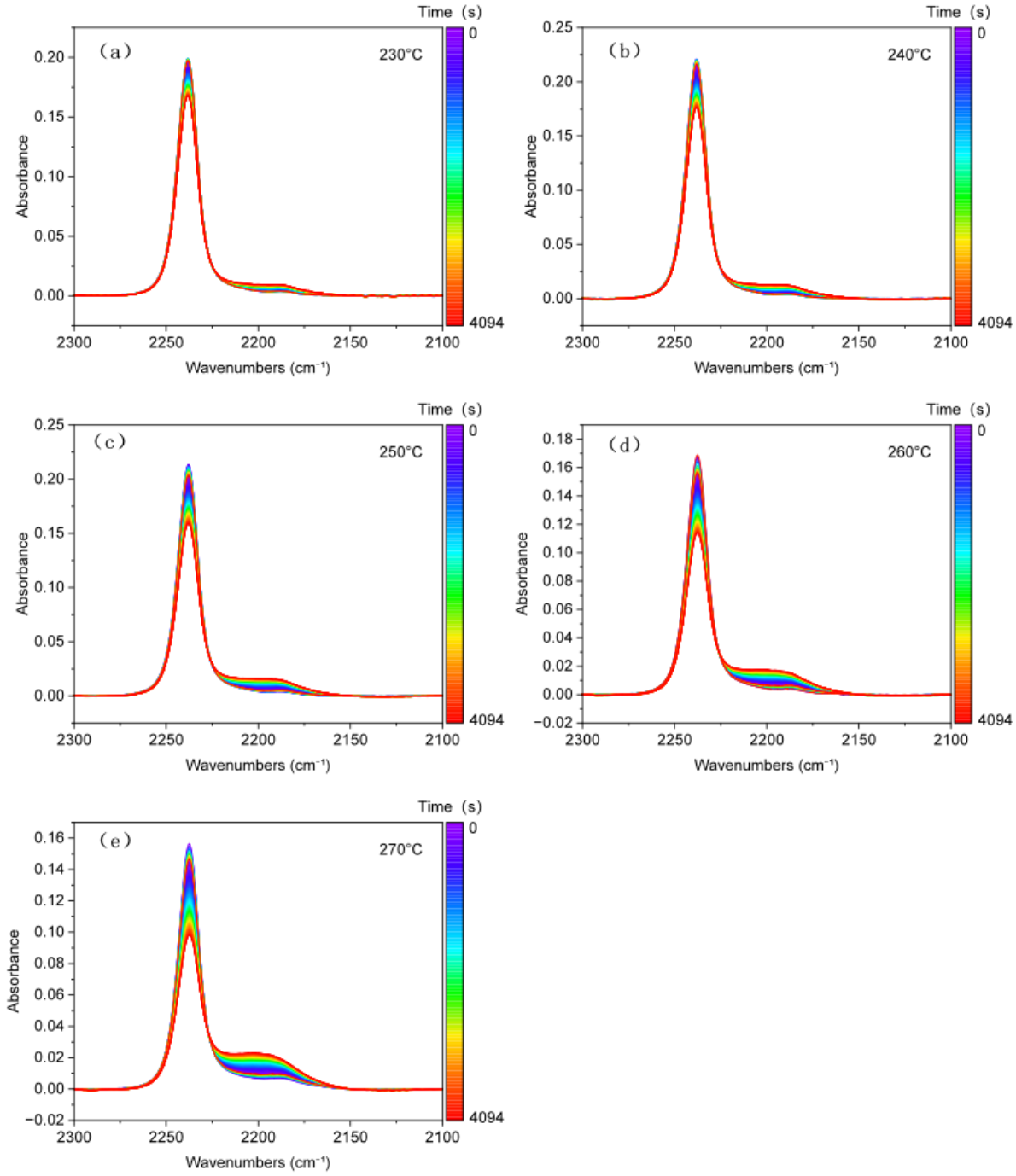

Figure 3: In-situ FTIR spectra of the nitrile characteristic peak region of PAN films during heat treatment at 230–270 °C under air atmosphere

3) Evolution of nitrile groups under the two different atmospheres

Compared with the spectra obtained under nitrogen atmosphere, the spectral evolution under air atmosphere exhibits pronounced differences, revealing that oxygen participation exerts a certain regulatory effect on the thermal stabilization behavior.

At the same temperature, the absorbance decay rate of the nitrile peak in air is noticeably slower than that in nitrogen. At 230 ℃, the initial dimensionless concentration in air is 0.2, and after 4094 s of heat treatment it decreases to 0.18; whereas in nitrogen, the initial value is 0.33, which declines to 0.24 after the same duration. At 250 ℃, the residual nitrile peak intensity in air after 4094 s is 0.16, while the same degree of decay is achieved much more rapidly in nitrogen. At a given temperature, the nitrogen atmosphere is more favorable for the conversion and consumption of nitrile groups, suggesting that the presence of oxygen actually inhibits the cyclization reaction. A possible explanation is that oxidation reactions in air compete with cyclization, consuming some active centers or reaction sites. Meanwhile, the oxygen-containing structures thus formed may impose steric hindrance on neighboring nitrile groups, impeding their further participation in cyclization. Furthermore, elevated temperatures promote the reaction under both atmospheres, but the reaction rate in nitrogen consistently remains higher than that in air, further confirming that an inert atmosphere is more conducive to revealing the intrinsic cyclization kinetics of PAN fibers.

Under nitrogen atmosphere, the nitrile characteristic peak remains relatively stable in the range of 230-260 ℃. It is not until 270 ℃ that a weak shoulder begins to appear near 2240 cm^{-1}. This indicates that, in the absence of oxygen, the cyclization reaction or the formation of conjugated structures requires a higher thermal driving force, and the reaction progress is correspondingly delayed. In contrast, under air atmosphere with oxygen participation, the evolution of the nitrile characteristic peak exhibits a lower onset temperature and more pronounced changes in peak shape. When the temperature reaches 250 ℃, a distinct shoulder begins to emerge on the higher-wavenumber side of the main peak. As the heat-treatment temperature increases, the intensity of this shoulder gradually grows, and the peak becomes sharper and more conspicuous. This phenomenon suggests that oxygen-involved reactions in air promote the consumption of nitrile groups and the generation of conjugated structures.

The participation of oxygen significantly alters the thermal stabilization behavior of PAN films. Oxygen can act both as an initiator for the cyclization reaction and as a direct reactant forming oxygen-containing functional groups, while simultaneously promoting dehydrogenation reactions.

4.2 Effect of Oxygen on the Apparent Rate Constant and Apparent Equilibrium Concentration

1) Evolution of the apparent rate constant and apparent residual concentration under nitrogen atmosphere

The apparent rate constant (k), apparent equilibrium concentration (y_∞), and the sum of squared residuals (SSR) for the two-parameter kinetic model under nitrogen atmosphere were obtained by solving the model using MATLAB. The relevant kinetic parameters are presented in Table 2 and Figure 4.

Table 2: Kinetic parameters obtained from the two-parameter model fitting at 230–270 °C under nitrogen atmosphere

T(℃)	k(s^{-1})	y_∞	SSR
230	0.00040809	0.69424698	0.000959518
240	0.00045173	0.64284558	0.001770174
250	0.00051808	0.54071009	0.002700575
260	0.00073978	0.42696625	0.007753364
270	0.0005825	0.40368243	0.006407505

From the experimental data presented above, the apparent rate constant k exhibits a clear trend of first increasing and then decreasing with rising temperature, identifying 260 ℃ as the optimal temperature region under the present experimental conditions, where k reaches its maximum and the apparent reaction rate is the highest. At this temperature, y∞has already dropped to a relatively low level, indicating a considerably high extent of nitrile conversion. This observation also provides a kinetic rationale for the industrial practice of employing a stepwise temperature-ramping protocol during pre-oxidation. In the low-temperature range of 230-250 ℃, the reaction remains well controllable and the model fitting precision is satisfactory. In the medium-to-high temperature range of 250-260 ℃, the reaction is accelerated and the depth of nitrile conversion is enhanced, while directly raising the temperature to 270 ℃ should be avoided, as it would lead to a decrease in reaction rate and an aggravation of side reactions.

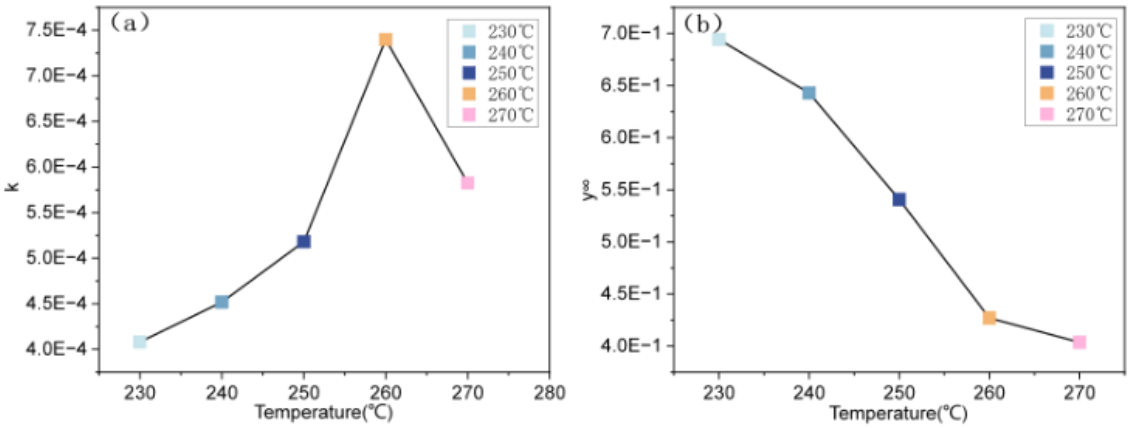

Figure 4: Temperature dependence of kinetic parameters under nitrogen atmosphere. (a) Apparent rate constant k as a function of temperature; (b) Dimensionless apparent residual nitrile concentration as a function of temperature

As shown in Figure 4(b), the apparent residual concentration exhibits a distinct temperature dependence. At all temperatures examined, the nitrile concentration does not decay to zero; instead, the dimensionless apparent residual nitrile concentration decreases monotonically with increasing temperature. Specifically, y_∞ is approximately 0.69 at 230 ℃, drops to 0.64 at 240 ℃, further decreases to 0.54 at 250 ℃, to 0.43 at 260 ℃, and finally to 0.40 at 270 ℃. This monotonic decline indicates that higher temperatures are more favorable for driving the nitrile-consuming reactions, resulting in less residual nitrile content within the same reaction period.

2) Evolution of the apparent rate constant and apparent residual concentration under air atmosphere

Under air atmosphere, the two-parameter kinetic model was employed to perform nonlinear fitting of the y_{CN}-t data. Table 3 summarizes the kinetic parameters obtained from the fitting along with the corresponding sum of squared residuals (SSR).

From Table 3, it can be observed that the apparent rate constant k initially increases and then decreases with increasing temperature. The k value at 250 ℃ under air atmosphere is significantly higher than that at the same temperature under nitrogen, whereas the k value at 270 ℃ is lower than that under nitrogen. This indicates that oxygen plays a dual role: at relatively low temperatures it promotes the cyclization reaction, while at higher temperatures it may inhibit further reaction progression, possibly due to the formation of a dense oxidized layer that hinders subsequent reactions.

This variation pattern suggests that oxygen exhibits a dual role during the thermal stabilization of PAN. In the low-temperature range of 230-250 ℃, the promoting effect of oxygen dominates, and the apparent reaction rate increases with temperature. When the temperature exceeds 250 ℃, the inhibitory effect of oxygen gradually becomes evident, leading to a decrease in the apparent reaction rate. This inhibition may be related to structural changes in the PAN films themselves or the occurrence of certain side reactions at elevated temperatures.

Table 3: Kinetic parameters obtained from the two-parameter model fitting at 230–270 °C under air atmosphere

T(℃)	k(s^{-1})	y∞	SSR
230	0.00038989	0.8473494	0.004281092
240	0.00042366	0.82605375	0.005344549
250	0.00074084	0.82470415	0.007763945
260	0.00071923	0.77599074	0.009388986
270	0.00039019	0.71821027	0.01163966

As shown in Figure 5, the apparent residual concentration decreases monotonically with increasing temperature, dropping from 0.8473494 at 230 ℃ to 0.71821027 at 270 ℃, indicating that elevated temperatures promote more thorough nitrile conversion and result in lower residual concentrations. Compared with the nitrogen atmosphere, the decrease in y∞ under air atmosphere is only 15%, whereas that under nitrogen is 42%. This discrepancy suggests that the temperature dependence of the apparent residual nitrile concentration is relatively weakened in air, which may be related to the competitive oxidation reactions.

From Table 3, it is also evident that the sum of squared residuals (SSR) increases progressively with temperature, reaching a minimum at 230 ℃ and rising to 0.01163966 at 270 ℃. This indicates that the fitting error of the two-parameter kinetic model accumulates as the temperature increases. Consequently, the model performs better in describing the kinetic behavior of PAN film pre-oxidation in the low-temperature range of 230-250 ℃, whereas its descriptive capability diminishes at higher temperatures, likely due to the increasing complexity of the reaction mechanisms under elevated temperatures.

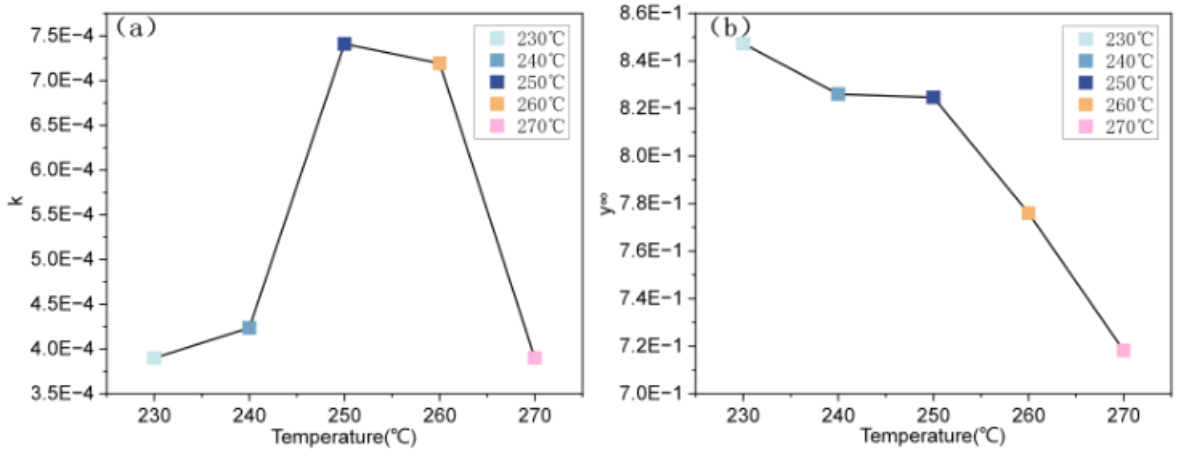

Figure 5: Temperature dependence of kinetic parameters under air atmosphere. (a) Apparent rate constant k as a function of temperature; (b) Apparent residual nitrile concentration as a function of temperature

4.3 Analysis of Apparent Activation Energy and Apparent Pre-exponential Factor

1) Analysis of apparent activation energy and apparent pre-exponential factor under nitrogen atmosphere

According to the Arrhenius equation, the relationship between the apparent rate constant k and temperature T can be linearly fitted in logarithmic form. By plotting ln k versus 1000/T, the Arrhenius plot shown in Figure 6 is obtained.

As seen in Figure 6, with the exception of a slight deviation of the data point at 270 °C, the remaining four temperature points (230 ℃, 240 ℃, 250 ℃, and 260 ℃) exhibit a relatively good linear relationship. Using MATLAB software, the apparent activation energy Ea under nitrogen atmosphere is

determined to be 27.56 kJ/mol, and the apparent pre-exponential factor A is 0.3. Combined with the results from the two-parameter model established above, it is likely that this model is more suitable for the low-temperature pre-oxidation stage. Therefore, after excluding the 270 °C data point, the re-evaluated apparent activation energy under nitrogen is 42.63 kJ/mol, and the apparent pre-exponential factor A is 10.3.

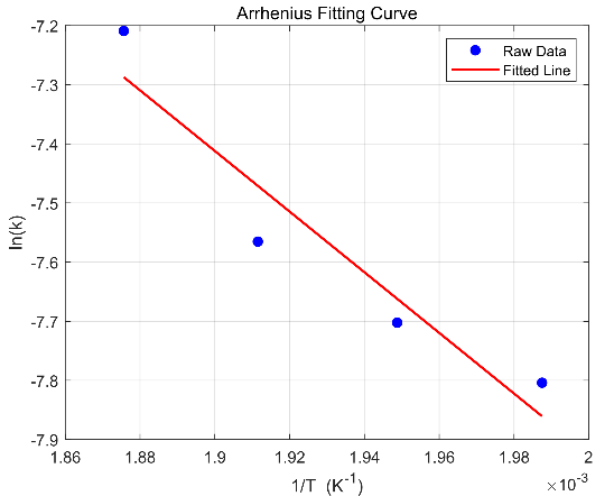

Figure 6: Arrhenius fitting curve for the cyclization reaction of PAN under nitrogen (2) Analysis of apparent activation energy and apparent pre-exponential factor under air atmosphereatmosphere

The apparent activation energy of 42.63 kJ/mol is in good agreement with the reported values for PAN cyclization in the range of 40-80 kJ/mol. The relatively low activation energy indicates that the cyclization of copolymeric PAN (containing itaconic acid) proceeds more readily than that of homopolymeric PAN, which is attributed to the carboxyl groups in itaconic acid that can initiate cyclization via an ionic mechanism.

Analysis of apparent activation energy and apparent pre-exponential factor under air atmosphere

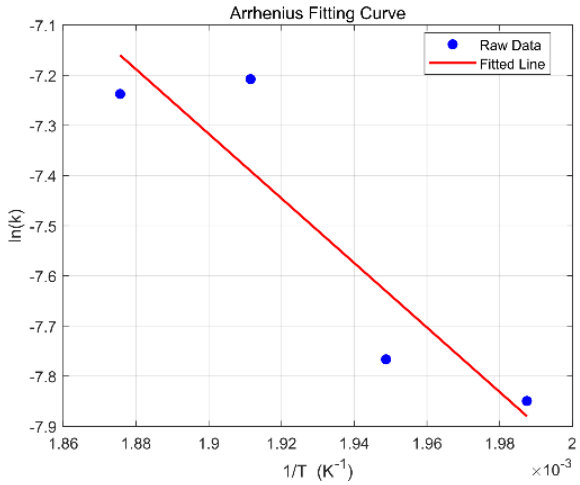

Figure 7: Arrhenius fitting curve for the cyclization reaction of PAN under air atmosphere.

As shown in Figure 7, the four experimental points are evenly distributed along the fitted straight line, exhibiting a reasonably good linear relationship with a linear correlation coefficient close to unity, indicating that ln k and 1/T strictly follow the Arrhenius relationship within the selected temperature range. This result verifies that the apparent kinetic behavior of the PAN cyclization reaction in the low-temperature region can be effectively described by the Arrhenius equation, and also suggests that the reaction mechanism remains relatively simple within this temperature interval, with negligible influence from side reactions. Using MATLAB software, the apparent activation energy Ea under air is determined to be 53.51 kJ/mol, and the apparent pre-exponential factor A is 136.

3) Comparative analysis of kinetic parameters under air and nitrogen atmospheres

Under identical experimental conditions, the kinetic parameters obtained in air atmosphere are all higher than those obtained in nitrogen atmosphere. In terms of apparent activation energy, the value under air (53.51 kJ/mol) is significantly higher than that under nitrogen (42.63 kJ/mol), with a difference of approximately 10.9 kJ/mol. This difference may be attributed to the fact that in nitrogen atmosphere, the reaction proceeds predominantly via pure thermal cleavage, mainly involving the cyclization of C≡N side groups or HCN elimination, for which the energy barriers of these elementary reactions are relatively low. In contrast, in air (oxidizing atmosphere), oxygen participates in the reaction, possibly through adsorption and activation to form oxygen-containing intermediates, thereby increasing the complexity of the reaction pathways and resulting in a higher apparent activation energy. The involvement of oxygen may also trigger competitive side reactions that alter the main reaction pathway, further raising the reaction energy barrier.

With regard to the apparent pre-exponential factor, the value under air (136) is substantially larger than that under nitrogen (10.3), differing by more than one order of magnitude. This is possibly due to the presence of oxygen in air, which increases the diversity of reaction pathways and allows more types of molecular collisions to lead to reaction events. Meanwhile, oxidation reactions may involve gas-solid or gas-liquid interfacial reactions, where the frequency of effective collisions at the interface is higher than that in the bulk phase, thus elevating the apparent pre-exponential factor. In addition, a compensation effect generally exists between the activation energy and the pre-exponential factor; reaction systems with higher activation energies tend to exhibit higher pre-exponential factors. In the present study, both the apparent activation energy and the apparent pre-exponential factor in air are higher than those in nitrogen, which is consistent with the general rule of the compensation effect. Although the reaction mechanism varies with the atmosphere, the kinetic parameters still maintain an intrinsic correlation. This result indicates that the presence of oxygen increases the apparent activation energy of the cyclization reaction, which is in agreement with the findings of Fitzer et al.

5. Conclusion

In this study, PAN films were employed as the research subject. Targeting the experimental phenomenon of residual nitrile concentration in the later stage of PAN pre-oxidation under isothermal and time-limited conditions, a two-parameter kinetic model for PAN pre-oxidation was

constructed. Using in-situ FTIR spectroscopy, the infrared spectral characteristics and kinetic differences of PAN films during isothermal heat treatment at various temperatures under both nitrogen and air atmospheres were systematically investigated, and the dual role of oxygen in the reaction was elucidated. This work provides a theoretical basis and experimental support for optimizing the pre-oxidation process of carbon fibers. The main findings are as follows:

1) By incorporating the experimental data and observed phenomena, the apparent rate constant k and apparent residual concentration y_∞ were introduced to establish the two-parameter kinetic model for PAN pre-oxidation. The kinetic parameters were solved using MATLAB software. The results show that the sum of squared residuals (SSR) gradually increases with rising temperature, yet remains on the order of 10^{-3}-10^{-4}, indicating that the overall fitting performance of the model is satisfactory. It is also found that the model exhibits a certain temperature dependence; higher temperatures introduce more complex reactions, leading to a moderate decrease in the model's descriptive accuracy for high-temperature systems.

2) Comparison of the apparent reaction rates reveals that the optimal temperature is 250 ℃ in air atmosphere and 260 ℃ in nitrogen atmosphere. The optimal temperature in air shifts downward by approximately 10 ℃ relative to that in nitrogen, suggesting that the presence of oxygen lowers the optimal reaction temperature, thereby enabling higher reaction efficiency at lower temperatures.

3) In both atmospheres, the apparent residual concentration decreases monotonically with increasing temperature. However, the values of $y\infty$ in air are consistently higher than those in nitrogen at each temperature, and the decrease with temperature is only 15% in air, compared with 42% in nitrogen. This indicates that oxygen may shift the reaction equilibrium toward a higher residual nitrile content, thereby inhibiting the cyclization reaction from achieving deep conversion.

4) The apparent activation energy in air is found to be higher than that in nitrogen, indicating more complex reaction pathways and an elevated energy barrier in the oxidative atmosphere. The apparent pre-exponential factor in air is substantially greater than that in nitrogen, implying that oxygen increases the frequency of effective molecular collisions and the diversity of reaction pathways.

5) The apparent rate constant initially increases and then decreases with rising temperature, further corroborating the dual-action mechanism of oxygen. Below 250 ℃, the promoting effect of oxygen dominates, accelerating the apparent reaction rate; above 250 ℃, the inhibitory effect gradually emerges, leading to a decrease in the reaction rate. This phenomenon arises from the fact that oxygen acts as an initiator to promote cyclization at lower temperatures, while at higher temperatures, the formation of a dense oxidized layer hinders further reaction progress..

Acknowledgments

This work was financially supported by the Science and Technology Development Plan Project of Jilin Province under Grant No.20230201121GX.

References

[1] Y. Ge (2021). Study on the structure and properties of PAN-based carbon fiber precursor during pre-oxidation and improvement of skin-core structure. Dissertation, Changchun University of Technology.

[2] T. Ishikawa, F. Tanaka, F. Uehara, et al. (2025). Mesoscopic structure with high aspect ratio in PAN-based carbon fibers. Carbon, vol.234, p.119-128.

[3] H. H. Hefni, N. Basiouny, Z. Abouelmagd, et al. (2022). Preparation of polyacrylonitrile with different molecular weights and high conversion yield in aqueous phase polymerization. Egyptian Journal of Chemistry, vol.65, (in press).

[4] N. L. T. Nguyen, C. Creighton, S. Nunna, et al. (2024). PAN-precursor to carbon fibre: An investigation of manufacture and material properties for varying comonomer composition. Polymer Degradation and Stability, vol.227, p.110-121.

[5] Y. F. Wang, Y. W. Wang, L. H. Xu, et al. (2021). Regulating the radial structure of polyacrylonitrile fibers during pre-oxidation and its effect on the mechanical properties of the resulting carbon fibers. New Carbon Materials, vol.36, no.4, p.827-834.

[6] X. Liu, W. Chen, Y. Hong, et al. (2015). Stabilization of atactic-polyacrylonitrile under nitrogen and air as studied by solid-state NMR. Macromolecules, vol.48, no.15, p.5300-5309.

[7] Y. Liu, P. Guo, Z. Guo, et al. (2025). A comparison study of the synergistic influence of discrepancy in exothermic behavior of polyacrylonitrile-based precursor fibers and the continuous gradient pre-oxidation condition on stabilization structure. Journal of Applied Polymer Science, vol.142, no.13, p.e56234.

[8] X. Gao, et al. (2025). Selective heterogeneous photocatalytic activation for toluene oxidation: recent advances. Chemical Synthesis, vol.5, p.100-112.

[9] Y. Hou, T. Sun, H. Wang, et al. (2008). Effect of heating rate on the chemical reaction during stabilization of polyacrylonitrile fibers. Textile Research Journal, vol.78, no.9, p.806-811.

[10] F. Panerai, T. Cochell, A. Martin, et al. (2019). Experimental measurements of the high temperature oxidation of carbon fibers. International Journal of Heat and Mass Transfer, vol.136, p.972-986.

[11] X. L. Yang, Q. F. Chen, G. J. Liu, et al. (2023). Effect of pre-oxidation temperature on properties of large-tow carbon fibers. Hi-Tech Fiber and Application, vol.48, no.4, p.29-32.

[12] Q. Gao, Z. Wang, Y. Zhou, et al. (2024). Effect of temperature gradient on the chemical structure and physical morphology of polyacrylonitrile fibers during thermal stabilization process. Polymer Degradation and Stability, vol.228, p.110-122.

[13] J. Zeng, J. Liu, G. Zhao, et al. (2023). Study on the structure evolution and temperature zone regulation mechanism of polyacrylonitrile fibers during pre-oxidation process. Iranian Polymer Journal, vol.32, no.12, p.1511-1522.

[14] H. Q. Song, Y. F. Wen, Y. G. Yang, et al. (2008). Kinetics of cyclization reaction of polyacrylonitrile fibers studied by DSC. Synthetic Fiber Industry, vol.31, no.3, p.1-4.
[15] X. Chen, H. Zhang, Y. Liu, et al. (2022). Effect of pre-oxidation time on structure and properties of polyacrylonitrile-based carbon fiber pre-oxidized fibers. New Chemical Materials, vol.50, no.4, p.5-9.
[16] J. Wang, Y. E. Ge, A. R. Chen, et al. (2024). Effect of pre-oxidation degree on structure and properties of polyacrylonitrile thermal oxidative stabilized fiber. China Plastics / Zhongguo Suliao, vol.38, no.11, p.78-83.
[17] B. Xu, J. J. Jin, J. Yan, et al. (2026). From PAN precursor to carbon fiber: Multi-stage stretching-mediated structure evolution and performance enhancement. Carbon Trends, vol.23, p.100627.
[18] L. Zoli, F. Servadei, F. Cicogna, et al. (2023). Enhancing PANox fiber properties through controlled oxidation and tensioning: A study on shrinkage inhibition and structural analysis. Polymer Degradation and Stability, vol.218, p.110574.