Molecular Dynamics Simulation Study on the Effects of Irradiation and Heat Treatment Sequence on the Molecular Structure of Pre-oxidized Polyacrylonitrile Fibers

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Abstract

Pre-oxidation is a critical step in the preparation of polyacrylonitrile-based (PAN) carbon fibers, and gamma irradiation represents an effective approach for optimizing the thermal pre-oxidation process. However, the effects and underlying mechanisms of gamma irradiation and thermal treatment sequencing on pre-oxidation remain unclear. To address this, the present study employs molecular dynamics simulation methods to analyze the influence of gamma irradiation and thermal treatment sequencing on structural changes during the pre-oxidation of PAN fibers, focusing on molecular chain morphology evolution, species variation, and reaction pathways. The results demonstrate that the irradiation-followed-by-heating (-T) treatment renders PAN molecular chain segments more stable, concentrates the types of pre-oxidation products, and promotes earlier generation of a greater number of radicals in PAN molecular chains, thereby accelerating cyclization, oxidation, cross-linking, and other reaction processes while achieving secondary cross-linking during heating, consequently enhancing the degree of pre-oxidation of PAN fibers. Conversely, the heating-followed-by-irradiation (T-) approach yields fewer radicals in PAN molecular chains during the thermal treatment stage, resulting in relatively fewer cross-linked structures, susceptibility to molecular chain scission during irradiation, and a diverse array of product types, ultimately leading to relatively inferior pre-oxidation outcomes. This study elucidates the mechanism through which gamma irradiation and thermal treatment sequencing affects the PAN fiber pre-oxidation process, providing theoretical support for structural regulation during PAN fiber pre-oxidation.

Full Text

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Abstract

Pre-oxidation is a critical step in the preparation of polyacrylonitrile-based (PAN) carbon fibers, and -irradiation serves as an effective means to optimize the heat treatment pre-oxidation process. However, the effects and underlying mechanisms of -irradiation and heat treatment sequence on pre-oxidation remain unclear. This study employs molecular dynamics simulation methods to analyze the influence of irradiation and heat treatment sequence on structural changes during the PAN fiber pre-oxidation process, focusing on molecular chain morphology evolution, species variation, and reaction pathways. The results demonstrate that the -irradiation followed by heating (-T) treatment approach yields more stable PAN molecular chain segment morphologies and more concentrated pre-oxidation product species. This method induces the formation of numerous free radicals earlier in the PAN molecular chains, thereby accelerating cyclization, oxidation, and cross-linking reactions while enabling secondary cross-linking during the heating process, ultimately enhancing the degree of PAN fiber pre-oxidation. Conversely, the heating followed by irradiation (T-) approach produces fewer free radicals during the heat treatment stage, resulting in relatively limited cross-linking structures. During subsequent irradiation, this leads to molecular chain scission, complicated product species, and consequently inferior final pre-oxidation effects. This research reveals the mechanism through which -irradiation and heat treatment sequence affect the PAN fiber pre-oxidation process, providing theoretical support for structural regulation during PAN fiber pre-oxidation.

Keywords: PAN pre-oxidation, irradiation, heat treatment, time-sequence, molecular dynamics simulation

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Carbon fibers are high-performance materials with carbon content exceeding 90%, widely applied across numerous fields due to their exceptional tensile strength and modulus [1, 2]. As the primary precursor for carbon fiber production, PAN fibers undergo key processing steps including pre-oxidation, carbonization, and graphitization [3, 4]. During the pre-oxidation stage, PAN precursor fibers experience cyclization, oxidation, dehydrogenation, cross-linking, and thermal decomposition reactions, accompanied by complex thermodynamic and mechanical property changes that ultimately form a stable ladder-like structure [5]. Consequently, the pre-oxidation process becomes crucial for determining carbon fiber quality. However, conventional heat treatment pre-oxidation suffers from non-uniform oxygen penetration, creating a radial skin-core structure in fibers that adversely affects the overall performance of the resulting carbon fibers [6-8].

In recent years, ionizing radiation technology has attracted considerable attention as an effective modification method for polymer materials and polymer modification [9-12]. Researchers have consequently introduced high-energy irradiation technology to optimize PAN fiber pre-oxidation. Liu et al. [13] investigated -ray irradiation of PAN fibers under vacuum conditions and its effect on pre-oxidation reactions. Their results demonstrated that -ray irradiation effectively reduced the initiation temperature of PAN fiber pre-oxidation reactions, significantly moderated the exothermic behavior during pre-oxidation, and accelerated the pre-oxidation process. Tan et al. [14] examined the structural changes in PAN precursor fibers induced by -ray irradiation, finding that irradiation reduced fiber crystallinity and crystallite size while promoting transformation of PAN fiber macromolecular chains into ladder structures, confirming that irradiation could enhance production efficiency, reduce energy consumption, and optimize PAN fiber structure and properties. Dang et al. [7] studied the effects of -ray irradiation on radial structural heterogeneity in PAN fibers during thermal stabilization, revealing that irradiated PAN fibers exhibited more uniform oxygen distribution and higher overall oxygen content during thermal stabilization, indicating that irradiation promoted stabilization reactions and effectively reduced radial structural heterogeneity after heat treatment pre-oxidation. Nevertheless, existing research has primarily focused on overall characterization of pre-oxidized PAN fibers, with insufficient exploration of the synergistic mechanism between irradiation and heat treatment. Furthermore, a clear and comprehensive understanding of the microscopic mechanisms underlying fiber structure evolution during PAN fiber pre-oxidation remains lacking.

Molecular dynamics simulation technology has garnered significant attention in recent years as a powerful tool for investigating material microscale behavior. Molecular dynamics can elucidate atomic-level reaction processes, including chemical bond formation and cleavage, as well as dynamic material behavior in various environments [15-17], providing a new perspective for comprehensive and precise investigation of microscopic mechanisms. To date, Shen et al. [18] have utilized molecular dynamics simulations to predict the molecular structure of crystalline layers in spun PAN fibers, concluding that quasi-crystalline chains with hexagonal crystal systems and 65% to 85% main-chain trans fractions represent suitable models for carbon fiber precursors. This finding indirectly validates the effectiveness of MD simulation methods for studying PAN fiber pre-oxidation feasibility. Yao et al. [19] established a model combining random chemical reactions with molecular dynamics to simulate in detail the atomic stabilization process of PAN chain segments. However, these simulation studies have primarily concentrated on PAN molecular model development, with limited progress in exploring irradiation and heat treatment processes.

In response, this study employs molecular dynamics simulation to construct a PAN molecular model using PKA (Primary Knock-on Atom) atom bombardment and gradient heating methods. Focusing on the irradiation and heat treatment processes during PAN pre-oxidation, we analyze the effects of irradiation and heat treatment sequence on PAN fiber structural evolution and final pre-oxidation efficacy from perspectives including molecular chain morphology changes, species distribution, and reaction pathways. These simulation results are validated through scanning electron microscopy and Fourier transform infrared spectroscopy analysis.

2.1.1 Construction of Molecular Chain Segments

This study employs Material Studio software to construct PAN molecular chain models based on the PAN fiber model presented by Shen et al. [18] and improved by introducing itaconic acid (IA) and methyl acrylate (MA), representing an industrially produced ternary polymer PAN molecular chain bundle. The molecular single chain consists of 2% IA, 3% MA, and 97% acrylonitrile copolymer [20] with syndiotactic configuration. The PAN chain bundle model is arranged according to a hexagonal crystal system structure [18]. The molecular monomers used in modeling are shown in Figures 1 Figure 1: see original paper-(c), with the PAN chain bundle model illustrated in Figures 1(d) (front view) and 1(e) (side view).

2.1.2 Pre-oxidation Environment Simulation

The PAN fiber pre-oxidation process occurs in an oxygen-containing environment. Liu et al. [21] investigated the effect of oxygen concentration in the pre-oxidation atmosphere on the radial structure distribution of PAN fibers and proposed optimal oxidation atmosphere conditions with oxygen volume concentration of 21.15%-21.34%. Therefore, this study constructed a box with dimensions of 208Å×120Å×120Å, containing a PAN molecular chain bundle (composed of 19 single chains) and 84 oxygen molecules to ensure a PAN fiber density of 1.2 g/cm³ and oxygen volume concentration of 21% [18], with oxygen randomly distributed around the molecular chain bundle to obtain the PAN pre-oxidation model for simulation experiments, as shown in Figure 2 [Figure 2: see original paper]. Since this study primarily focuses on the effects of irradiation and heat treatment sequence on the microscopic dynamics of PAN molecular chains during pre-oxidation, introducing oxygen flow or replenishment mechanisms would require additional coupling with fluid dynamics models to simulate oxygen convection and diffusion, significantly increasing simulation system complexity. Consequently, this study establishes oxygen as a static environmental variable, adding 84 oxygen molecules to the box without subsequent replenishment during the pre-oxidation process to maintain constant concentration. This approach controls for a single variable to clearly identify the independent effects of irradiation and heating sequence on pre-oxidation reaction kinetics.

2.1.3 Simulation Parameter Settings

All models in this study employ periodic boundary conditions, with molecular chain bundles distributed along the x-axis. To simulate stress between continuous fibers, two regions with 2.5Å thickness were defined at both ends of the molecular bundle on the YOZ plane (as shown in Figure 3 [Figure 3: see original paper]), with atoms in these regions fixed to ensure axial alignment and prevent scattering of the molecular bundle. The model subsequently underwent energy minimization and relaxation processes, with energy minimization performed using the Conjugate Gradient Method [22] and relaxation conducted under NVT ensemble conditions at 300K, using an integration time step of 0.25 fs for 40,000 steps.

For the irradiation process, this study simulates -irradiation through PKA atom interactions with PAN molecular chains. At an irradiation absorption dose of 100 kGy (1 kGy = 1 J/g), the PKA energy collision parameter is 2.5 keV (1 keV = 1.6×10^{1} J, where keV is an energy unit representing kiloelectronvolts). Five oxygen atoms were designated as PKA atoms, positioned at (30,2,65), (60,2,65), (108,2,65), (152,2,65), and (183,2,65) in the simulation box. Based on the kinetic energy formula $E=\frac{1}{2}mv^2$, each oxygen atom velocity was calculated as 0.797381 Å/fs and set to impact PAN molecular chains along the positive y-axis direction [23]. The irradiation process was conducted under NVE ensemble to ensure constant total energy transfer from PKA atoms to the molecular chain bundle, simulated with an integration step of 0.25 fs for 80,000 steps, totaling 20 ps duration. During this process, PKA atoms transfer their carried energy to the molecular chain bundle, inducing chemical bond cleavage in PAN molecular chains, detachment of atoms or atomic groups, and generation of chain radicals.

The heating process employed gradient temperature elevation under NVT ensemble: 443K-463K-483K-503K-523K-543K-563K-583K-603K, with temperature increments of 20K. Each gradient consisted of two stages: temperature ramping followed by isothermal holding [6], with each stage using an integration step of 0.25 fs for 40,000 steps, lasting 10 ps. The heating process utilized a Nose-Hoover thermostat to ensure temperature uniformity throughout the system. The entire simulation process employed an accelerated algorithm for equilibrium, adjusting the potential energy surface in the potential function to enable high-energy barrier processes that are difficult to overcome in conventional simulations to occur more frequently, thereby accelerating the simulation process and allowing short-duration simulations to describe reaction processes in actual industrial conditions.

In this study, oxygen atoms serve as PKA atoms, effectively avoiding introduction of other heteroatoms. Since PAN molecular chains form chain radicals through hydrogen atom abstraction and can undergo oxidation reactions by combining with oxygen, this study further employs the number of atoms or atomic groups detached from molecular chains to indirectly describe free radical quantities, and uses the number of oxygen molecules consumed within the system to describe the degree of oxidative cross-linking. Based on different pre-oxidation sequences, the model with irradiation followed by heating is designated as the -T group, while the heating followed by irradiation model is designated as the T- group. Simulation calculations and visualization were completed using the open-source tools LAMMPS and OVITO, respectively.

2.2.1 Experimental Materials and Equipment

The materials and equipment required for this experiment are listed in Tables 1 and 2.

Table 1 Relevant parameters of experimental materials and reagents

Material/Reagent Name	Source
PAN precursor fiber	Jilin Tangu Carbon Fiber Co., Ltd.
Methyl acrylate	Shanghai Macklin Biochemical Technology Co., Ltd.

Table 2 Experimental apparatus and their models

Equipment	Model	Manufacturer
Muffle furnace	KF1200	Tianjin Mafu’ er Technology Co., Ltd.
Field emission scanning electron microscope	GeminiSEM500	Carl Zeiss AG, Germany
Fourier transform infrared spectrometer	Nicolet iS50	Thermo Fisher Scientific

2.2.2 Irradiation Treatment

PAN precursor fibers and heat-treated PAN fibers were subjected to -ray irradiation in air atmosphere at Beijing Hongyi Sifang Radiation Technology Co., Ltd., using a Co radiation source. The irradiation dose rate in this study was 2.7 kGy/h, with irradiation time adjusted to modify the dose. Based on previous reports, lower doses can significantly improve the structure of pre-oxidized fibers and effectively enhance the mechanical properties of resulting carbon fibers. Therefore, this study employed an absorption dose of 100 kGy for both PAN precursor fibers and heat-treated fibers.

2.2.3 Heating Process

PAN fiber heat treatment was conducted in a muffle furnace. During heating, fibers were fixed at the furnace top with a weight suspended below the fiber bundle to apply a traction force of 5N. The fiber bundle specification was 12K with an average diameter of 12.54 m. The heating process employed gradient heating with temperature intervals and gradients consistent with the simulation experiments. Individual temperature ramping and isothermal holding periods were each 5 minutes, with the entire heating process lasting 105 minutes. PAN fibers after irradiation and heat treatment were designated as -PAN and T-PAN, respectively. T-PAN and -PAN after subsequent irradiation and heating were designated as T- -PAN and -T-PAN, respectively.

3.1 Effect of Irradiation and Heat Treatment Sequence on Molecular Chain Morphology Evolution During Pre-oxidation

Figures 4 [Figure 4: see original paper] and 5 [Figure 5: see original paper] display the dynamic changes in the -T-PAN (irradiation followed by heating) and T- -PAN (heating followed by irradiation) molecular models during pre-oxidation, respectively. The results indicate that sequence differences between irradiation and heat treatment significantly affect the efficacy of PAN pre-oxidation. In the -T-PAN group, PAN molecular chains undergo dehydrogenation reactions upon absorbing irradiation energy, generating randomly distributed free radicals (Figures 4b-c). Subsequently, during the heating stage, rising temperatures enhance molecular chain thermal motion while accompanied by small molecule evolution (Figures 4d-i). In contrast, the T- -PAN group first initiates preliminary reactions in PAN molecular chains through thermal effects, generating only small quantities of free radicals locally and resulting in slow reaction rates (Figures 5b-j). When entering the irradiation stage, irradiation-induced radicals react on the basis of the heat-treated molecular chains. Due to limited local cyclization and cross-linking formed during the preliminary heating stage, the molecular chains exhibit only modest strength enhancement while flexibility decreases, leading to non-uniform energy transfer during high-energy irradiation that ultimately causes molecular chain scission and substantial hydrogen atom abstraction (Figures 5k-l). Consequently, PAN molecular chains in the T- -PAN system demonstrate lower stability compared to the -T-PAN system.

3.2 Effect of Irradiation and Heat Treatment Sequence on Species Distribution During Pre-oxidation

To elucidate the reasons for molecular chain morphology evolution during different pre-oxidation sequences, this section statistically analyzes changes in all species types and total species quantities within the simulation box during -T and T- pre-oxidation processes. For clarity of presentation and analysis, only data from the isothermal heating process totaling 100 ps were statistically analyzed.

Figure 6 [Figure 6: see original paper] shows the changes in molecular quantities and species types during pre-oxidation for both systems. In the -T-PAN group, both species number and molecular quantity increase significantly due to high-energy irradiation causing dehydrogenation or chain scission in PAN molecular chains, generating various chain radicals and imine radicals that increase molecular species and quantities. During subsequent heating, molecular quantities and species numbers remain relatively stable with minor fluctuations because cross-linking formed by irradiation stabilizes molecular chains, preventing destruction during heat treatment. Meanwhile, thermal decomposition during heating leads to small molecule release and partial intermolecular cross-linking, causing fluctuations in species types and molecular quantities. In the T- -PAN group, molecular quantities and species numbers change slowly and continue increasing during the initial heating stage because oxidation and cyclization occur during heat treatment without main chain destruction, while some small molecules are released or partial chain scission occurs, creating a sustained growth trend. During subsequent irradiation, molecular quantities and species types increase rapidly, likely due to high-energy radiation inducing radical formation again. The limited cross-linking structures formed during heating result in modest strength enhancement of the PAN molecular chain bundle while chain flexibility remains restricted, causing PAN molecular chain damage during energy transfer and generating numerous molecules. At the end of pre-oxidation, the T- -PAN group exhibits higher species numbers but lower molecular quantities than the -T-PAN group, indicating that heating followed by irradiation produces more heterogeneous pre-oxidation products, which hinders subsequent carbon fiber performance enhancement.

3.3 Effect of Irradiation and Heat Treatment Sequence on Molecular Cross-linking and Small Molecule Formation During Pre-oxidation

To further monitor specific changes in species types and quantities during pre-oxidation, this section performs classified statistical analysis of species types to examine the reaction kinetics of radical formation through dehydrogenation, oxidative cross-linking, and chain scission defect formation in both -T-PAN and T- -PAN groups. The classification results are presented in Table 3 , with statistical results for major species quantities shown in Figure 7 [Figure 7: see original paper].

Table 3 Species classification results and categories

Species Category	Description
C H N O	Original PAN molecular chain

Species Category	Description
C O<8	Molecular chains with 300-313 main-chain carbon atoms and fewer than 8 oxygen atoms
C O>8	Molecular chains with 300-313 main-chain carbon atoms and more than 8 oxygen atoms
C>313, C<300, C<13	Molecular chains with >313, 13-300, or <13 main-chain carbon atoms
CO, CO , HCN, NH	Carbon- and nitrogen-containing gas molecules
H O, H, O	Water molecules, hydrogen atoms, oxygen molecules

In the -T-PAN group (Figure 7a), the original molecular chain C H N O begins to lose large quantities of H atoms and small molecular groups under high-energy irradiation, forming C O<8. Some molecular chains continue to decompose and undergo oxygen-free cross-linking to produce cross-linked products such as C>313 and C O>8, while large molecular chains primarily decompose into C<300 molecular chains and C<13 small molecular segments during irradiation. Small molecules including CO, CO , HCN, NH , and H O appear during irradiation, indicating that dehydrogenation and cyclization have already begun in the molecular chains. During the heating stage, O quantities gradually decrease while C<13 quantities increase and C<300 quantities slightly decrease. This occurs because numerous chain radicals formed on the PAN molecular chain bundle during irradiation provide abundant reaction sites for oxygen, promoting oxidative cross-linking. The cross-linked structures enhance the thermal stability of the molecular chain bundle, preventing excessive pyrolysis of PAN molecular chains during heating. Decreasing H atom quantities and increasing HCN, NH , and H O quantities indicate that small molecule generation occurs concurrently with H atom participation during pre-oxidation.

In the T- -PAN system (Figure 7b), the quantity of original molecular chains C H N O decreases only slightly during the heating stage, producing minimal H atoms. Oxygen consumption also remains low during this phase, indicating that insufficient radical sites are generated on PAN molecular chains during initial heating, preventing timely oxygen participation. The minimal increase in C<13, C<300, HCN, NH , and H O quantities suggests that molecular chains remain relatively intact while pre-oxidation reactions proceed slowly. Upon entering the irradiation process, H atom and C<13 quantities increase substantially because the limited cross-linking structures formed during heating cannot withstand and transfer irradiation energy, causing PAN molecular chains to undergo dehydrogenation and chain scission. Comparing the two groups, irradiation followed by heating can effectively generate free radicals first through irradiation, accelerating oxygen participation and significantly reducing the temperature required for reaction initiation during heating. In contrast, the heating followed by irradiation process requires higher temperatures to generate free radicals and initiate pre-oxidation reactions with lower frequency, while subsequent irradiation energy damages structures formed during heating, resulting in poorer pre-oxidation effects compared to the -T-PAN group.

3.4 Analysis of Pre-oxidation Reaction Pathways Under Different Irradiation and Heat Treatment Sequences

To precisely illustrate the PAN pre-oxidation process, this study employs ReacNetGenerator to statistically analyze bond connectivity relationships of PAN molecules during simulation and examine the primary reaction mechanisms in both systems. Combined with visualization and species analysis, we investigate atomic migration, reaction transformation processes, and structural information of reaction products and intermediate fragments during PAN pre-oxidation in both groups. For convenient presentation, these processes are described and illustrated using chemical structural formulas, where dots represent radical sites. The results are as follows:

Figure 8 [**Figure 8: see original paper**] Formation of chain radicals

As shown in Figure 8, chain radicals (alkyl radicals) form when -C-H groups on the PAN molecular main chain lose H atoms during irradiation or heating. These alkyl radicals subsequently undergo addition reactions with adjacent molecular chain -C N groups, forming imine radicals. In Figure 7 from Section 3.3, the numbers of H atoms abstracted from PAN molecular chains in the -T-PAN group during irradiation and heating are 27 and 3, respectively, while in the T- -PAN group, the numbers are 1 and 204 during heating and irradiation, respectively. This indicates that radical formation occurs primarily during the irradiation stage, with earlier irradiation producing more radicals.

Figure 9 [**Figure 9: see original paper**] Cyclization and cross-linking of molecular chains. In the figure, (a) represents the cyclization reaction, and (1), (2), (3), (4) in (b) represent the cross-linking reactions.

PAN molecular chain cyclization is primarily radical-dependent. As shown in Figure 9(a), when a -C N group ionizes to form a -C=N • radical, the nitrogen atom in this radical combines with a neighboring sp-hybridized carbon to form a cyclic structure. The -C=N • radical then propagates along the molecular chain, continuing to initiate cyclization reactions.

The first cross-linking process of molecular chains occurs through two primary types. As shown in Figure 9(b)(1) and (2), oxygen-free cross-linking involves direct intermolecular chain cross-linking through radical sites. In oxygen-participating cross-linking processes shown in Figure 9(b)(3) and (4), molecular chains first form oxygen radicals that cross-link through ether bonds or undergo addition reactions with adjacent chain -C N groups to form imine radical cross-links. Radical formation is a prerequisite for both cross-linking types. In Figure 7 from Section 3.3, the quantities of C O>8 and C>313 at the end of pre-oxidation are 4 and 2, respectively, in the -T-PAN group, while both are 0 in the T- -PAN group, demonstrating that prior irradiation promotes cross-linking during pre-oxidation by forming more radicals.

Figure 10 [**Figure 10: see original paper**] Oxidation reaction and secondary cross-linking. In the figure, (a) represents the oxidation reaction, and (b) represents the secondary cross-linking reaction.

The oxidation reaction mechanism proceeds in two stages. As shown in Figure 10(a), PAN molecular chains form -OH groups in an oxygen atmosphere, subsequently undergoing secondary oxidation to generate epoxy bridge structures and carbonyl groups [24], reactions that also require abundant radical sites. In Figure 10(b), further pre-oxidation enables molecular chains to form numerous cyclic structures and oxygen-containing hydrophilic groups. These groups undergo condensation and dehydration reactions to form cross-links again, increasing the degree of cross-linking in PAN molecular chains [25]. Additionally, in Figure 7 from Section 3.3, the remaining oxygen molecule counts in the box at the end of pre-oxidation are 36 and 71 for the -T-PAN and T- -PAN groups, respectively, proving that irradiation generates more radical sites in molecular chains, accelerates molecular chain reactions, facilitates oxygen participation, and promotes the pre-oxidation process. Therefore, irradiation followed by heating promotes the formation of oxygen-containing groups on molecular chains and increases the degree of cross-linking in PAN molecular chains.

Figure 11 [**Figure 11: see original paper**] Pyrolysis and damage of molecular chains. In the figure, (a) represents the pyrolysis reaction of molecular chains, and (b) represents the damage reaction of molecular chains.

Additionally, PAN molecular chain damage and pyrolysis accompany the pre-oxidation process. As shown in Figure 11(a), this reaction primarily occurs in the -T-PAN system. At the beginning of irradiation, molecular chains remain relatively independent without cross-linking, allowing irradiation energy to transfer effectively through molecular chains. Consequently, few short PAN molecular chains form during irradiation, while uncyclized portions undergo pyrolysis during subsequent heating, forming partial short chains again. As shown in Figure 11(b), during the heating stage of the T- -PAN system, limited molecular chain radicals and oxidative cross-linking result in insufficient capacity to withstand and transfer high energy during subsequent irradiation, causing molecular chains to release large quantities of H atoms and form more short chains. In Figure 7 from Section 3.3, the C<13 quantities at the end of pre-oxidation are 57 and 161 for the -T-PAN and T- -PAN groups, respectively, indicating that heating followed by irradiation causes greater damage to PAN molecular chains and is detrimental to pre-oxidation outcomes.

3.5.1 Fiber Surface Morphology Validation Analysis

Figure 12 [Figure 12: see original paper] Fiber surface morphology

As shown in Figure 12, scanning electron microscopy observation of fiber surface morphology reveals that surface groove characteristics in precursor fibers are preserved in pre-oxidized fibers. Compared with PAN precursor fibers, -PAN fibers exhibit smoother surfaces, indicating that irradiation treatment effectively removes surface contamination layers and reduces defects. In contrast, pre-oxidized fibers prepared with different irradiation and heat treatment sequences (-T-PAN and T- -PAN) display more numerous and deeper surface grooves compared to T-PAN, attributed to more significant oxidation reactions occurring in the fiber surface layer. Compared with T- -PAN, -T-PAN fibers exhibit more regular surface grooves, indicating that the irradiation-followed-by-heating treatment approach promotes pre-oxidation reactions while effectively reducing fiber damage.

3.5.2 Infrared Spectroscopy Validation Analysis

Figure 13 [Figure 13: see original paper] (a, b) FTIR spectra

Through Fourier transform infrared spectroscopy analysis, this study investigates the effects of -ray irradiation combined with heat treatment pre-oxidation processes on the chemical structure evolution of PAN fiber materials. As shown in Figure 13a, PAN precursor fibers after irradiation treatment exhibit attenuated characteristic peaks at 2245 cm ^{1}, 2940 cm ^{1}, and 1400 cm ^{1} (corresponding transmittance values changing from 95.7, 96.4, 96.9 to 96.6, 96.9, 97.8, respectively), confirming decreased contents of C N, C-H, and -CH functional groups. Simultaneously, enhanced absorption peaks at 1730 cm ^{1} and 1628 cm ^{1} (corresponding transmittance values changing from 97.1, 98 to 96.3, 97.1, respectively) reveal increased contents of C=O, C=N, and C=C groups. These spectral data demonstrate that PAN precursor fibers undergo cyclization, dehydrogenation, and oxidation reactions under -irradiation [26].

The infrared spectral characteristics of heat-treated pre-oxidized fibers, shown in Figure 13b, exhibit distinct characteristic peaks at 2240 cm ^{1}, 1660 cm ^{1}, 1560 cm ^{1}, 1463 cm ^{1}, 1360 cm ^{1}, 1280 cm ^{1}, and 950 cm ^{1}, corresponding to C N, C=O, C=C and C=N conjugated structures, -CH, -CH , C-O-C, and -CH groups in C=C-C=C [24,27]. Compared with PAN precursor fibers, pre-oxidized fibers after heat treatment show significant differences in chemical structure, most notably the near-complete disappearance of C N groups (corresponding transmittance changing from 96.2 to 98.7). Compared with T-PAN, -T-PAN and T- -PAN exhibit higher contents of C=C and C=N conjugated systems (corresponding transmittance changing from 99.2 to 97.6 and 98.3, respectively) and -CH groups (corresponding transmittance changing from 97.2 to 96.5 and 96.2, respectively), confirming more significant cyclization and dehydrogenation reactions [27]. Additionally, -T-PAN and T- -PAN contain richer oxygen-containing cross-linked structures, attributed to oxidation reactions induced by -irradiation in air atmosphere, promoting increased C-O-C bonds in T- -PAN (corresponding transmittance changing from 97.1 to 96.2), while increased C-O-C bonds in -PAN are preserved in the final pre-oxidized fibers. In T- -PAN, the -CH content in C=C-C=C structures decreases significantly (corresponding transmittance changing from 98 to 98.6), while -CH content increases (corresponding transmittance changing from 96.9 to 96.2), because -irradiation simultaneously promotes both cross-linking and scission processes [24]. C-H bonds in C=C-C=C structures generate carbon radicals through irradiation-induced cleavage, subsequently forming cross-links that optimize the ladder structure. Meanwhile, C-C bond scission also leads to increased -CH groups. Overall, the synergistic effect of radiation and heat treatment significantly enhances the degree of PAN fiber pre-oxidation, with -T-PAN exhibiting higher pre-oxidation degree than T- -PAN.

This study employs molecular dynamics simulation to investigate the effects of -irradiation and heat treatment sequence on the PAN pre-oxidation process, revealing the mechanism through which irradiation and heat treatment sequence affects PAN pre-oxidation efficacy from perspectives including molecular chain morphology evolution, species changes, and reaction pathways. Simulation results are validated through fiber surface morphology analysis and infrared spectroscopy, leading to the following conclusions:

1. The irradiation-followed-by-heating (-T-PAN) approach yields more stable molecular chain segment morphologies. Irradiation generates numerous uniformly distributed free radicals in PAN molecular chains, enabling the formation of more cross-linked structures during heating that enhance molecular chain strength and stability.

2. The irradiation-followed-by-heating (-T-PAN) synergistic treatment produces more concentrated pre-oxidation product species. Radicals and cross-linked structures generated during the irradiation stage maintain molecular chain integrity during heat treatment, resulting in uniform products. In contrast, heating-followed-by-irradiation (T- -PAN) produces limited cross-linked structures during the heating stage, resulting in low molecular chain strength that leads to molecular chain damage during subsequent irradiation and heterogeneous product species, which is detrimental to fiber performance improvement.

3. The irradiation-followed-by-heating (-T-PAN) process can generate more free radicals earlier on PAN molecular chains, accelerating cyclization, cross-linking reactions, and oxygen-containing group formation, promoting deep pre-oxidation and achieving secondary cross-linking that enhances cross-linking degree. Conversely, heating-followed-by-irradiation (T- -PAN) fails to generate sufficient radical sites during the heating stage, causing molecular chains to be unable to withstand irradiation energy during subsequent irradiation and resulting in more molecular chain scission.

These research findings explain from a microscopic perspective the effects and mechanisms of irradiation and heat treatment sequence on the PAN pre-oxidation process, confirming that the irradiation-followed-by-heating pre-oxidation process is superior to the heating-followed-by-irradiation process. This provides theoretical guidance for enhancing PAN pre-oxidation degree and producing high-performance carbon fibers in industrial applications.

Author Contributions: Miao Tengfei was responsible for experiment implementation, data processing and analysis, and initial manuscript drafting and revision; Shao Ruiqi was responsible for overall research design; Wu Meng participated in experiments and partial data processing; Liu Shouguo and Ma Tianshuai provided methodological guidance; Wang Wei, Li Tianyu, and Shi Haiting performed proofreading and language editing; Xu Zhiwei served as the primary supervisor and manuscript reviewer. All authors have read and approved the final manuscript.

References: [1] Chand S J. Review Carbon fibers for composites[J]. Journal of Materials Science, 2000, 35(6):1303-1313. [2] Jiang B, Zhang T, Zhao L, et al. Interfacially reinforced carbon fiber composites by grafting modified methylsilicone resin[J]. Composites Science & Technology, 2017, 140(MAR.1):39-45. [3] Mao Q, Rajabpour S, Kowalik M, et al. Predicting cost-effective carbon fiber precursors: Unraveling the functionalities of oxygen and nitrogen-containing groups during carbonization from ReaxFF simulations[J]. Carbon, 2020, 159: [4] Rahaman M S A, Ismail A F, Mustafa A. A review of heat treatment on polyacrylonitrile fiber[J]. Polymer Degradation and Stability. 2007, 92(8): [5] Warner S, Peebles L, Uhlmann D. Oxidative stabilization of acrylic fibres. I. II[J]. Stabilization dynamics. 1979. Oxygen uptake and general model. DOI:10.1007/BF00551029. [6] Sun L H, Shang L, Xiao L H, et al. The influence of stabilization efficiency on skin–core structure and properties of polyacrylonitrile fibers[J]. Journal of Materials Science, 2020, 55(8): 3408-18. [7] Dang W, Liu J, Huang X Y, et al. Effects of gamma-Ray Irradiation on the Radial Thermal Polyacrylonitrile during Fibers Structure Heterogeneity Stabilization[J]. Polymers, 2018, 10(9): 943. [8] Shao R Q, Zhou Z D, Wang W, et al. Reinforcement of carbon fibers: -irradiation induced microporous modulation and surface defect repairing with graphene quantum dots[J]. Journal of Physics D: Applied Physics, 2024, 57(15): [9] Wang Daoxi, Shi Haiting, Liu Shengkai, et al. Effect of electron beam irradiation on the structure of Ta-doped lithium-lanthanum-zirconium-oxygen (Li . La Zr . Ta . O) solid electrolytes[J]. Journal of Radiation Research and Radiation Processing, 2024, 42(1): 010206. DOI: 10.11889/j.1000-3436.2023-0077. [10] Dong Yingjie, Shi Haiting, Wang Shuo, et al. Synthesis of nitrogen-doped graphyne/iron catalysts via -ray irradiation and their properties[J]. Journal of Radiation Research and Radiation Processing, 2024, 42(1):010201. DOI:10.11889/j.1000-3436.2023-0075. [11] Zhang Y H, Huang Y D, Liu L, et al. Surface modification of aramid fibers with -ray radiation for improving interfacial bonding strength with epoxy resin[J]. Journal of Applied Polymer Science. 2007, 106(4): 2251-62. [12] Li Y, Gao J C. Preparation of silicon nitride ceramic fibers from polycarbosilane fibers by -ray irradiation curing[J]. Materials Letters, 2013, 110: 102-4. [13] Liu W H, Wang M H, Xing Z, et al. Radiation-induced crosslinking of polyacrylonitrile fibers and the subsequent regulative effect on the pre-oxidation process[J]. Radiation Physics and Chemistry, 2012. DOI:10.1016/j.radphyschem. [14] Tan L J, Wan A J. Structural changes of polyacrylonitrile precursor fiber induced by -ray irradiation[J]. Materials Letters, 2011, 65(19-20): 3109-11. [15] Saha B, Schatz G C. Carbonization in polyacrylonitrile (PAN) based carbon fibers studied by ReaxFF molecular dynamics simulations[J]. The Journal of Physical Chemistry B, 2012, 116(15): 4684-92. [16] Mudedla S K, Vuorte M, Veijola E, et al. Effect of oxidation on cellulose and water structure: a molecular dynamics simulation study[J]. Cellulose, 2021, 28(7): 3917-33. [17] Sohail T, Nakarmi S, Sweat R, et al. Simulation of surface asperities on a carbon fiber using molecular dynamics and fourier series decomposition to predict interfacial shear strength in polymer matrix composites[J]. Composite Interfaces, 2022, 29(8): 947-70. [18] Shen T T, Li C Y, Haley B, et al. Crystalline and pseudo-crystalline phases of Implications for carbon fiber polyacrylonitrile from molecular dynamics: precursors[J]. Polymer, 2018, 155: 13-26. [19] Yao S K, Li C Y, Jackson M, et al. Molecular Modeling of Stabilization during Processing of Polyacrylonitrile-Based Carbon Fibers[J]. Macromolecules, 2024, 57(12): 5578-88. [20] Sun L H, Li M, Shang L, et al. The influence of oxygen on skin-core structure of polyacrylonitrile-based precursor fibers[J]. Polymer, 2020, 197(8):122516. [21] Liu Jie, Ouyang Xinfeng, Lian Feng, et al. Effect of Oxidative Stabilization Atmosphere on the Radial Structure of Polyacrylonitrile Fibers During Their Conversion to Carbon Fibers[J]. Acta Polymerica Sinica. 2012,(11):1326-1334. [22] Ashraf C, Vashisth A, Bakis C E, et al. Reactive Molecular Dynamics the Atomic Oxygen Impact on Epoxies with Different Simulations of Chemistries[J]. The Journal of Physical Chemistry C, 2019, 123(24): 15145-56. [23] Li T Y, Shao R Q, Shi H T, et al. Heterogeneous microstructure of -irradiated pre-oxidized PAN fiber revealed by microfocus SR-SAXS reconstruction and molecular simulation[J]. 2024, The Journal of Chemical Physics, 2024, 161(12): [24] Zhao W Z, Lu Y G, Zhou L X, et al. Effects on the oriented structure and mechanical properties of carbon fibers by pre-irradiating polyacrylonitrile fibers with gamma ray[J]. Journal of Materials Science. 2016, 51(15): 7073-84. [25] Zhao W Z, Lu Y G, Jiang J Q, et al. The effect of -ray irradiation on the microstructure and thermal properties of polyacrylonitrile fibers[J]. RSC Advances, 2015, 5(30): 23508-18. [26] Liu Jianhua, Zhang Cheng, Guo Shenghui, et al. Advances in the Pre-oxidation Process During the Preparation of Polyacrylonitrile-Based Carbon Fibers[J]. Journal of Kunming University of Science and Technology: Natural Science Edition. 2018, 43(04): 20-9. [27] Nunna S, Naebe M, Hameed N, et al. Investigation of progress of reactions and evolution of radial heterogeneity in the initial stage of thermal stabilization of PAN precursor fibres[J]. Polymer Degradation and Stability. 2016, 125: 105-14.

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