Effect of Irradiation and Heat Treatment Timing on the Molecular Structure of Pre-oxidized Polyacrylonitrile Fibers: A Molecular Dynamics Simulation Study

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Abstract

Pre-oxidation is a critical step in the preparation of polyacrylonitrile-based (PAN) carbon fibers, and γ-irradiation is an effective means for optimizing the thermal pre-oxidation process. However, the effects and mechanisms of the timing sequence between γ-irradiation and heat treatment on pre-oxidation remain unclear. To address this, this study employs molecular dynamics simulation methods to analyze the influence of the timing sequence of γ-irradiation and heat treatment on the structural changes during the pre-oxidation process of PAN fibers from the perspectives of molecular chain morphology evolution, species variation, and reaction pathways. The results demonstrate that the treatment method of irradiation followed by heating (γ-T) renders the PAN molecular chain segments more stable in morphology, results in more concentrated species of pre-oxidation products, and this approach can induce the earlier generation of a larger number of free radicals in the PAN molecular chains, thereby accelerating the reaction processes of cyclization, oxidation, cross-linking, etc., and achieving secondary cross-linking during the heating process, consequently enhancing the degree of pre-oxidation of PAN fibers. In contrast, the treatment method of heating followed by irradiation (T-γ), due to the limited formation of free radicals in the PAN molecular chains during the heat treatment stage, results in relatively fewer cross-linked structures, and is prone to causing molecular chain scission during the irradiation process, leading to a diverse and complex array of product species, resulting in relatively inferior final pre-oxidation outcomes. This study reveals the mechanism of action of the timing sequence between γ-irradiation and heat treatment on the pre-oxidation process of PAN fibers, providing theoretical support for structural regulation during the pre-oxidation process of PAN fibers.

Full Text

Molecular Dynamics Simulation of the Effect 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 (PAN)-based carbon fibers, and γ-irradiation serves as an effective method for optimizing the heat treatment pre-oxidation process. However, the effects and underlying mechanisms of γ-irradiation and heat treatment sequence on pre-oxidation remain unclear. This study employs molecular dynamics simulation to analyze how the sequence of γ-irradiation and heat treatment influences structural changes during PAN fiber pre-oxidation, focusing on molecular chain morphology evolution, species transformation, and reaction pathways. The results demonstrate that the irradiation-followed-by-heating (γ-T) approach yields more stable PAN molecular chain segments and more concentrated pre-oxidation products. This method induces a greater number of free radicals earlier in the PAN molecular chains, thereby accelerating cyclization, oxidation, and cross-linking reactions while enabling secondary cross-linking during heating, ultimately enhancing the degree of PAN fiber pre-oxidation. Conversely, the heating-followed-by-irradiation (T-γ) approach generates fewer free radicals during the heat treatment stage, resulting in relatively limited cross-linking structures. Subsequent irradiation causes molecular chain scission and yields complex product mixtures, leading to inferior pre-oxidation outcomes. This research elucidates the mechanism by which γ-irradiation and heat treatment sequence affects 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

Introduction

Carbon fibers are high-performance materials with carbon content exceeding 90%, widely utilized across numerous fields due to their exceptional tensile strength and modulus [1, 2]. Polyacrylonitrile (PAN) fibers serve as the pri-

mary precursor for carbon fiber production, with the manufacturing process involving key steps of pre-oxidation, carbonization, and graphitization [3, 4]. During pre-oxidation, PAN precursor fibers undergo cyclization, oxidation, dehydrogenation, cross-linking, and thermal decomposition reactions, accompanied by complex thermodynamic and mechanical property changes that ultimately form a stable ladder 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 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 [9-12]. Researchers have consequently introduced high-energy irradiation techniques to optimize PAN fiber pre-oxidation. Liu et al. [13] investigated γ-ray irradiation of PAN fibers under vacuum and its effect on pre-oxidation reactions, finding that γ-irradiation effectively reduced the initiation temperature of PAN fiber pre-oxidation, significantly moderated the exothermic behavior during pre-oxidation, and accelerated the overall process. Tan et al. [14] examined structural changes in PAN precursor fibers induced by γ-ray irradiation, observing decreased crystallinity and crystallite size that facilitated transformation of PAN macromolecular chains into ladder structures, thereby 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 γ-ray irradiation on radial structural heterogeneity during thermal stabilization of PAN fibers, demonstrating 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 pre-oxidation. However, existing research has primarily focused on overall characterization of pre-oxidized PAN fibers, with limited investigation into the synergistic mechanisms 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 new perspectives for comprehensive and precise investigation of microscopic mechanisms. To date, Shen et al. [18] utilized molecular dynamics simulations to predict the molecular structure of spun PAN crystalline layers, revealing that quasi-crystalline chains with hexagonal crystal systems and 65% to 85% backbone 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. Yao et al. [19] developed a combined model of random chemical reactions and molec-

ular dynamics to simulate the atomic stabilization process of PAN segments in detail. However, these simulation studies have primarily focused 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 PAN molecular models using Primary Knock-on Atom (PKA) bombardment and gradient heating methods. Focusing on the irradiation and heat treatment processes during PAN pre-oxidation, we analyze how the sequence of these treatments affects PAN fiber structure evolution and final pre-oxidation outcomes from the perspectives of molecular chain morphology changes, species distribution, and reaction pathways. Scanning electron microscopy and Fourier transform infrared spectroscopy analyses further validate the simulation results.

2.2.1 Construction of Molecular Chain Segments

This study constructed PAN molecular chain models using Material Studio software, based on the PAN fiber model presented by Shen et al. [18] and improved by introducing itaconic acid (IA) and methyl acrylate (MA) to create an industrially produced ternary polymer PAN molecular chain bundle. The molecular single chain was synthesized from 2% itaconic acid (IA), 3% methyl acrylate (MA), and 97% acrylonitrile [20] in a syndiotactic configuration. The PAN chain bundle model was arranged according to a hexagonal crystal system structure [18]. The molecular monomers used in modeling are shown in [Figure 1: see original paper] (a), (b), and (c), while the PAN chain bundle model is presented in [Figure 1: see original paper] (d) (main view) and (e) (side view).

2.2.2 Construction of Pre-oxidation Models

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 structural distribution of PAN fibers and proposed optimal oxidation atmosphere conditions with oxygen volume concentrations of 21.15%-21.34%. Accordingly, this study constructed a simulation 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/cm^3 and an oxygen volume concentration of 21% [18]. The oxygen molecules were randomly distributed around the molecular chain bundle, yielding the PAN pre-oxidation model for simulation experiments, as shown in [Figure 2: see original paper]. Since this study primarily focuses on the influence of irradiation and heat treatment sequence on PAN fiber structure during pre-oxidation, the effects of oxygen flow and replenishment were not considered. Therefore, after adding 84 oxygen molecules to the box, no additional oxygen was supplied during pre-oxidation to maintain constant concentration.

2.2.3 Simulation Parameter Settings

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

For the irradiation process, interactions between high-energy Primary Knock-on Atoms (PKA) and PAN molecular chain bundles were simulated. This study utilized the same irradiation dose and corresponding PKA atom energy as Li et al. [23], specifically an irradiation absorbed dose of 100 kGy with PKA collision energy parameters of 2.5 keV. Five oxygen atoms were designated as PKA atoms, positioned at coordinates (30,2,65), (60,2,65), (108,2,65), (152,2,65), and (183,2,65) in the simulation box, and given initial velocities (0.797381 Å/fs along the positive y-direction) to impact the PAN molecular chain bundle. 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, corresponding to a total duration of 20 ps. During this process, PKA atoms transferred 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 increase under NVT ensemble: 443K-463K-483K-503K-523K-543K-563K-583K-603K, with temperature increments of 20K. Each gradient consisted of two stages: heating followed by isothermal holding [6], with each stage using an integration step of 0.25 fs for 40,000 steps (10 ps duration). The Nose-Hoover thermostat controlled system temperature to ensure uniformity.

In this study, oxygen atoms served as PKA atoms to effectively avoid introducing foreign impurity atoms. To facilitate observation of radical quantities and molecular chain oxidation cross-linking degree, the number of detached atoms or atomic groups from molecular chain bundles was used to indirectly describe radical quantities, while the number of consumed oxygen molecules in the system described the degree of oxidation cross-linking. Based on different pre-oxidation sequences, the irradiation-followed-by-heating model was designated as the γ-T group, and the heating-followed-by-irradiation model as the T-γ 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 and .

2.2.2 Irradiation Treatment

PAN precursor fibers and heat-treated PAN fibers were irradiated with γ-rays in air atmosphere at Beijing Hongyi Sifang Radiation Technology Co., Ltd. using a 60Co radiation source. The irradiation dose rate was 2.7 kGy/h, with dose adjusted by varying irradiation time. 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 irradiation dose of 100 kGy for both PAN precursor 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 tensile force of 5N. The heating process employed gradient heating: 170°C-190°C-210°C-230°C-250°C-270°C-290°C-310°C-330°C, with temperature gradients of 20°C and both heating and isothermal stages lasting 5 minutes each. The total heating process lasted 105 minutes. PAN fibers after irradiation and heat treatment were named γ-PAN and T-PAN, respectively, while T-PAN and γ-PAN after subsequent irradiation and heating were designated T-γ-PAN and γ-T-PAN, respectively.

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

[Figure 4: see original paper] and [Figure 5: see original paper] present dynamic changes in the two molecular models (γ-T-PAN: irradiation followed by heating; T-γ-PAN: heating followed by irradiation) during pre-oxidation. The results indicate that the sequence of irradiation and heat treatment significantly affects PAN pre-oxidation efficacy. In the γ-T-PAN group, PAN molecular chains underwent dehydrogenation reactions by absorbing irradiation energy, generating randomly distributed free radicals ([Figure 4: see original paper] b-c). Subsequently, during heating, increased temperature enhanced molecular chain thermal motion accompanied by small molecule evolution ([Figure 4: see original paper] d-i). In contrast, the T-γ-PAN group first initiated preliminary reactions in PAN molecular chains through thermal effects, generating only a small number of localized free radicals and resulting in slow reaction rates ([Figure 5: see original paper] b-j). When entering the irradiation stage, irradiation-induced radicals reacted on the basis of heat-treated molecular chains. Since the preliminary heating produced only localized cyclization and cross-linking, molecular chain strength improved minimally while flexibility decreased, leading to non-uniform energy transfer during subsequent high-energy irradiation that ultimately caused molecular chain scission and significant hydrogen atom detachment ([Figure 5: see original paper] k-l). Consequently, PAN molecu-

lar chains in the T-γ-PAN system exhibited lower stability compared to the γ-T-PAN system.

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

To elucidate the reasons for morphology changes in PAN molecular chains during irradiation and heating pre-oxidation, this study statistically analyzed the types and quantities of all species throughout each temperature stage of irradiation and heat treatment. For clarity, only data from the isothermal heating processes (totaling 100 ps) were statistically analyzed. [Figure 6: see original paper] a and b illustrate changes in molecular quantities and species types during pre-oxidation for both systems. In the γ-T-PAN group, both species variety and molecular quantity increased significantly due to high-energy irradiation causing dehydrogenation or chain scission in PAN molecular chains, generating various chain radicals and imine radicals. During subsequent heating, molecular quantities and species numbers remained relatively stable with minor fluctuations because the cross-linked structures formed by irradiation stabilized molecular chains, preventing destruction during heat treatment. Meanwhile, thermal decomposition released small molecules and some intermolecular cross-linking occurred, causing fluctuations in species variety and molecular quantity. In contrast, the T-γ-PAN group exhibited slow and continuous increases in molecular quantity and species variety during the initial heating stage, as thermal treatment induced oxidation and cyclization without destroying the molecular backbone while releasing some small molecules or causing partial chain scission. During the subsequent irradiation stage, molecular quantities and species types increased rapidly, likely because high-energy radiation induced radical formation again, while the limited cross-linking structures formed during heating provided insufficient strength and restricted chain flexibility, causing PAN molecular chain damage during energy transfer and generating numerous fragments. At the end of pre-oxidation, the T-γ-PAN group showed higher species numbers but lower molecular quantities than the γ-T-PAN group, indicating that heating followed by irradiation produces more heterogeneous pre-oxidation products, which hinders subsequent carbon fiber performance improvement.

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 study conducted classified statistical analysis of reaction species, with classification results shown in and quantitative statistics presented in [Figure 7: see original paper].

In the γ-T-PAN group ([Figure 7: see original paper] a), the original molecular chain C313H320N100O8 began detaching numerous H atoms and small molecu-

lar groups under high-energy irradiation to form C300-313O<8. Some molecular chains continued decomposing and underwent oxygen-free cross-linking to produce cross-linked products such as C>313 and C300-313O>8. By the end of irradiation, large molecular chains primarily decomposed into C<300 molecular chains and C<13 small molecular segments. During irradiation, small molecules including CO, CO2, HCN, NH3, and H2O began appearing, indicating that dehydrogenation and cyclization had already initiated during the irradiation stage. Entering the heating stage, O2 quantities gradually decreased while C<13 quantities increased and C<300 quantities slightly decreased. This occurred because numerous chain radicals formed on PAN molecular chain bundles during irradiation, providing sufficient reaction sites for oxygen and promoting oxidation cross-linking. The resulting cross-linked structures enhanced thermal stability of the molecular chain bundles, preventing excessive pyrolysis of PAN molecular chains during heating. Meanwhile, decreasing H atom quantities and increasing HCN, NH3, and H2O quantities demonstrated that small molecule generation occurred throughout pre-oxidation with H atom participation.

In the T-γ-PAN system ([Figure 7: see original paper] b), the original molecular chain C313H320N100O8 decreased only slightly during heating, generating minimal H atoms and consuming little oxygen. This indicated that the preliminary heating stage could not generate sufficient radical sites on PAN molecular chains for timely oxygen participation, while minimal increases in C<13, C<300, HCN, NH3, and H2O quantities suggested that molecular chains remained relatively intact but pre-oxidation reactions proceeded slowly. Upon entering the irradiation stage, quantities of H atoms and C<13 increased because the limited cross-linking structures formed during heating could not withstand and transfer irradiation energy, causing PAN molecular chain dehydrogenation and scission. Comparing both groups, irradiation followed by heating can effectively generate radicals first through irradiation, accelerating oxygen participation and reducing the temperature required for reactions during heating. Conversely, heating followed by irradiation requires higher temperatures to generate radicals and initiate pre-oxidation reactions with lower frequency, while subsequent irradiation energy damages structures formed during heating, yielding inferior pre-oxidation results compared to the γ-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 employed ReacNetGenerator to statistically analyze bond connectivity during simulation and examine the main reaction mechanisms of PAN pre-oxidation in both systems. Combined with visualization and species analysis, atomic migration and reaction transformation processes were investigated. For clarity, these processes are described using chemical structural formulas, where dots represent radical sites.

As shown in [Figure 8: see original paper], during irradiation or heating, H atoms detach from -C-H groups on the PAN molecular backbone to form chain

radicals (alkyl radicals), which then undergo addition reactions with adjacent -C N groups to form imine radicals. Formation of these two radical types primarily occurs during the irradiation stage, with earlier irradiation producing more radicals.

PAN molecular chain cyclization is closely related to radical formation. As shown in [Figure 9: see original paper] (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 mainly through two types, as shown in [Figure 9: see original paper] (b) (1) and (2). In oxygen-free cross-linking, molecular chains directly cross-link through radical sites. In oxygen-participating cross-linking, as shown in [Figure 9: see original paper] (b) (3) and (4), molecular chains first form oxygen radicals that cross-link through ether bonds or undergo addition reactions with -C N groups on adjacent chains to form imine radical cross-links. Since radical formation is a prerequisite for both cross-linking types, prior irradiation can promote cyclization and cross-linking during pre-oxidation by generating more radicals.

The oxidation reaction mechanism occurs in two stages. As shown in [Figure 10: see original paper] (a), PAN molecular chains form -OH groups in an oxygen atmosphere, subsequently undergoing secondary oxidation to generate epoxy bridge and carbonyl structures [24]. Such reactions also require numerous radical sites. As shown in [Figure 10: see original paper] (b), further pre-oxidation enables molecular chains to form numerous cyclic structures and oxygen-containing hydrophilic groups. These groups undergo condensation and dehydration reactions, forming cross-links again and increasing the cross-linking degree of PAN molecular chains [25]. Irradiation can generate more radical sites on molecular chains, accelerating reactions and facilitating the pre-oxidation process. Therefore, irradiation followed by heating promotes formation of oxygen-containing groups on molecular chains and increases the cross-linking degree of PAN molecular chains.

Additionally, PAN molecular chain damage and pyrolysis accompany the pre-oxidation process. As shown in [Figure 11: see original paper] (a), such reactions primarily occur in the γ-T-PAN system. At the beginning of irradiation, molecular chains were not yet cross-linked and remained relatively independent, allowing irradiation energy to transfer effectively through the molecular chains. Therefore, few short PAN molecular chains formed during irradiation, while during subsequent heating, uncyclized portions of molecular chains with lower heat resistance underwent pyrolysis, forming some short chains again. As shown in [Figure 11: see original paper] (b), during the heating stage of the T-γ-PAN system, limited molecular chain radicals and oxidation cross-linking resulted in insufficient capacity to withstand and transfer high energy during subsequent irradiation, causing molecular chains to release numerous H atoms and form more short chains. Thus, heating followed by irradiation causes greater damage

to PAN molecular chains and yields inferior pre-oxidation results.

3.5.1 Validation Analysis of Fiber Surface Morphology

Scanning electron microscopy observation of fiber surface morphology ([Figure 12: see original paper]) revealed that surface groove characteristics in precursor fibers were preserved in pre-oxidized fibers. Compared with PAN precursor fibers, γ-PAN fibers exhibited smoother surfaces, indicating that irradiation treatment effectively removed surface contamination layers and reduced defects. Pre-oxidized fibers prepared with different irradiation and heat treatment sequences (γ-T-PAN and T-γ-PAN) showed more numerous and deeper surface grooves compared to T-PAN, attributed to more significant oxidation reactions occurring on fiber surfaces. Compared with T-γ-PAN, γ-T-PAN fibers displayed more regular surface grooves, demonstrating that irradiation followed by heating not only promotes pre-oxidation reactions but also effectively reduces fiber damage.

3.5.2 Validation Analysis by Infrared Spectroscopy

Fourier transform infrared spectroscopy was employed to investigate the effects of γ-ray irradiation combined with heat treatment pre-oxidation on the chemical structure evolution of PAN fiber materials. As shown in [Figure 13: see original paper] a, PAN precursor fibers after irradiation treatment exhibited intensity attenuation of characteristic spectral peaks at 2245 cm^{-1}, 2940 cm^{-1}, and 1400 cm^{-1}, confirming decreased contents of C N, C-H, and -CH_2 functional groups. Simultaneously, enhanced absorption peaks at 1730 cm^{-1} and 1628 cm^{-1} revealed increased contents of C=O, C=N, and C=C groups. These spectral data demonstrate that PAN precursor fibers underwent cyclization, dehydrogenation, and oxidation reactions under γ-irradiation [26].

Infrared spectral characteristics of pre-oxidized fibers after heat treatment ([Figure 13: see original paper] b) showed distinct 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, conjugated C=C and C=N structures, -CH, -CH_2, C-O-C, and -CH groups in C=C-C=C structures [24, 27]. Compared with PAN precursor fibers, pre-oxidized fibers after heat treatment exhibited significant chemical structural differences, most notably the near-complete disappearance of C N groups. Compared with T-PAN, both γ-T-PAN and T-γ-PAN demonstrated higher contents of conjugated C=C and C=N systems and -CH groups, confirming more significant cyclization and dehydrogenation reactions [27]. Additionally, γ-T-PAN and T-γ-PAN contained richer oxygen-containing cross-linked structures due to oxidation reactions induced by γ-irradiation in air atmosphere, which increased C-O-C bonds in T-γ-PAN while the increased C-O-C bonds in γ-PAN were preserved in the final pre-oxidized fibers. In T-γ-PAN, -CH content in C=C-C=C structures decreased significantly while -CH_2 content increased because γ-irradiation simultaneously promoted both cross-linking and scission processes [24]. C-H bonds in C=C-C=C structures fractured under irradiation to gen-

erate carbon radicals that formed cross-links, optimizing the ladder structure, while C-C bond scission also led to increased -CH_2 groups. Overall, synergistic radiation and heat treatment significantly enhanced PAN fiber pre-oxidation degree, with γ-T-PAN exhibiting higher pre-oxidation degree than T-γ-PAN.

Conclusions

This study investigated the effects of γ-irradiation and heat treatment sequence on the PAN pre-oxidation process using molecular dynamics simulation, revealing the mechanism of sequence effects on pre-oxidation efficacy from perspectives of molecular chain morphology evolution, species transformation, and reaction pathways. Fiber surface morphology and infrared spectroscopy analyses validated the simulation results, leading to the following conclusions:

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

2. The irradiation-followed-by-heating (γ-T-PAN) synergistic treatment produces more concentrated PAN molecular chain pre-oxidation product species. Radicals and cross-linked structures generated during irradiation maintain molecular chain integrity during heat treatment, yielding uniform products. Conversely, heating-followed-by-irradiation (T-γ-PAN) produces limited cross-linked structures during heating, resulting in low molecular chain strength and subsequent irradiation-induced damage that creates complex product mixtures detrimental to fiber performance improvement.

3. The irradiation-followed-by-heating (γ-T-PAN) process generates 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. In contrast, heating-followed-by-irradiation (T-γ-PAN) fails to generate sufficient radical sites during heating, causing molecular chains to fracture under subsequent irradiation energy due to inability to withstand and transfer the energy effectively.

These findings facilitate microscopic understanding of the effects and mechanisms of irradiation and heat treatment sequence on the PAN pre-oxidation process, promote application of irradiation and molecular simulation technologies in pre-oxidation processes, and provide theoretical guidance for fiber structure regulation during PAN pre-oxidation.

Author Contributions

Miao Tengfei conducted the experiments, processed and analyzed data, and drafted and revised the manuscript; Shao Ruiqi designed the overall research; Wu Meng participated in experiments and partial data processing; Liu Shouguo and Ma Tianshuai provided methodological guidance; Wang Wei, Li Tianyu, and Shi Haiting proofread and edited the language; Xu Zhiwei served as the principal supervisor and reviewed the manuscript. All authors have read and approved the final text.

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Note: Figure translations are in progress. See original paper for figures.