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Thermodynamic Properties of the Interface in Carbon Fiber/Epoxy Resin Matrix Composites: A Molecular Dynamics Simulation Approach

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ABSTRACT

Carbon fiber/epoxy resin matrix composites have gained widespread application in aerospace, automotive, and electronics industries due to their excellent mechanical properties, lightweight characteristics, and corrosion resistance. However, due to the significant difference in thermal expansion coefficients between carbon fibers and the epoxy resin matrix, these composites are prone to thermal stresses during temperature changes, which can adversely affect their mechanical properties and long-term stability. Therefore, investigating the thermodynamic properties of the composite interface, especially the thermal expansion behavior and the evolution of interface thermal stresses, is of great theoretical and practical significance. Current studies on the thermodynamic properties of carbon fiber/epoxy resin matrix composites' interfaces primarily employ theoretical analysis, experimental testing, and numerical simulations. However, due to the complex microstructure of the composites, existing research methods have limitations in capturing the interface-level thermal stress and thermal expansion characteristics. In particular, traditional finite element analysis methods are unable to precisely capture thermal stresses and expansion properties at the interface level. To address this, molecular dynamics simulation, as a fine-scale research tool, effectively simulates the micro-level interactions within composites and provides more accurate predictions of thermodynamic properties. This study uses molecular dynamics simulations to explore the thermal expansion properties and interface thermal stresses of carbon fiber/epoxy resin matrix composites, revealing the thermodynamic behavior at the interface level. By integrating finite element analysis and cohesive zone model (CZM), this paper further conducts multi-scale simulations of the interface thermodynamic properties, systematically studying the evolution of thermal stresses and their impact on interface failure. This research not only provides a theoretical basis for a deeper understanding of the thermodynamic behavior of composites but also offers important references for optimizing the design and application of composite materials.

1. INTRODUCTION

With the continuous development of modern industrial technology, carbon fiber/epoxy resin matrix composites have been widely applied in aerospace, automotive, sports equipment, and electronic products due to their excellent mechanical properties, low density, and good corrosion resistance [1-4]. Especially in the field of high-performance composites, carbon fiber-reinforced plastics (CFRP) have become an ideal choice to replace traditional metal materials because of their high strength and lightweight characteristics [5-9]. However, the interface properties of composites, especially the thermodynamic behavior of the interface, directly affect their overall mechanical performance and long-term durability. Due to the significant difference in thermal expansion coefficients between carbon fibers and the epoxy resin matrix, thermal stresses can develop during temperature changes, which may lead to interface failure, material cracking, or even structural damage [10-14]. Therefore, studying the thermodynamic properties of carbon fiber/epoxy resin matrix composites, particularly the evolution of interface thermal stresses, is of great scientific significance and practical value for enhancing their performance and reliability.

Currently, some progress has been made in the study of the thermodynamic properties of the interface in carbon fiber/epoxy resin matrix composites. Through theoretical analysis, experimental measurements, and numerical simulations, scholars have conducted preliminary studies on the thermal expansion properties, interface thermal stresses, and thermal failure mechanisms of composite materials [15-18]. However, due to the complex microstructure and multi-scale properties of the materials, traditional research methods still face challenges in fully revealing the thermodynamic behavior of the composite interface, especially in the accurate calculation of interface thermal stresses and the prediction of thermal expansion properties at the micro-scale [19-23]. Therefore, conducting more refined molecular dynamics simulations not only provides a more accurate predictive tool

for interface thermodynamic behavior but also helps understand the interface failure mechanism, providing theoretical support for the design of new high-performance composite materials.

Among the existing research methods, experimental testing is limited by the material preparation process and experimental environment, making it difficult to precisely control variables and achieve high-resolution observation of local structures. Traditional numerical simulation methods, such as finite element analysis, also have limitations when dealing with complex micro-interface behaviors. Specifically, finite element methods often rely on macroscopic assumptions when considering the thermal expansion and thermal stresses at the composite material interface, neglecting the real interactions at the micro-level. This simplification leads to deviations in the simulation results, failing to fully reflect the thermodynamic response of the actual material under different temperature changes. Therefore, there is an urgent need for an advanced research method that can accurately capture molecular-scale interactions and effectively simulate the distribution of thermal expansion and thermal stresses.

The purpose of this study is to deeply analyze the thermodynamic properties of the interface in carbon fiber/epoxy resin matrix composites through molecular dynamics simulation technology, focusing on the material's thermal expansion behavior and the evolution of its interface thermal stresses. First, we will systematically explore the thermal expansion characteristics and thermal stress distribution of the composite materials at different temperatures based on molecular dynamics simulation methods, revealing the thermodynamic response mechanism at the carbon fiber and epoxy resin matrix interface. Then, by combining finite element analysis and CZM, we will carry out multi-scale simulations of the interface thermodynamic properties to further study the thermal stress and failure behavior at the interface level. These studies will contribute to a deeper understanding of the composite materials' interface properties and provide a theoretical basis for designing more efficient and reliable carbon fiber-reinforced composite materials, thus promoting their application in aerospace and other high-tech fields.

2. THERMAL EXPANSION PROPERTIES AND INTERFACE THERMAL STRESS ANALYSIS

In constructing the thermal expansion model for carbon fiber/epoxy resin matrix composites, it is necessary to carefully consider the thermodynamic and mechanical behavior of the materials under high-temperature conditions. In high-temperature environments, the thermal expansion characteristics, plastic behavior, and changes in interface thermal stresses of both the epoxy resin matrix and carbon fibers can significantly impact the macroscopic mechanical properties of the composites. Therefore, in order to accurately describe these changes, we must introduce temperature-sensitive factors into the thermal expansion model and comprehensively consider the anisotropy of the epoxy resin matrix and carbon fibers, along with their respective thermal expansion behaviors. Figure 1 shows the schematic diagram of the experimental setup used in this study for material thermal response testing.

The thermal expansion characteristics of the epoxy resin matrix at high temperatures are temperature-dependent, especially near its glass transition temperature. As the temperature increases, the molecular chain segments of the epoxy resin matrix become more active. After reaching the glass transition temperature, its thermal expansion coefficient increases sharply, mainly due to the increase in the degree of freedom of the chain segments caused by the glass transition of the material. Generally, the thermal expansion coefficient of the epoxy resin matrix exhibits a significant nonlinear change before and after the glass transition temperature. Before the glass transition temperature, it shows a linear increase, while after the glass transition temperature, a large expansion occurs. At high temperatures, the mechanical properties of the epoxy resin matrix also decrease significantly, and its modulus and yield strength may be notably affected. Therefore, the thermal expansion coefficient of the epoxy resin matrix under high-temperature conditions requires special attention, and fine modeling of its changes before and after the glass transition temperature is necessary. To simplify the calculation, in this section, it is assumed that the thermal expansion coefficient of the epoxy resin matrix varies linearly within the glass transition temperature range in the numerical simulation process, avoiding complex nonlinear thermal expansion models. This assumption has certain feasibility and practicality for numerical simulations. Figure 2 shows the variation of the thermal expansion coefficient of the epoxy resin matrix with temperature.

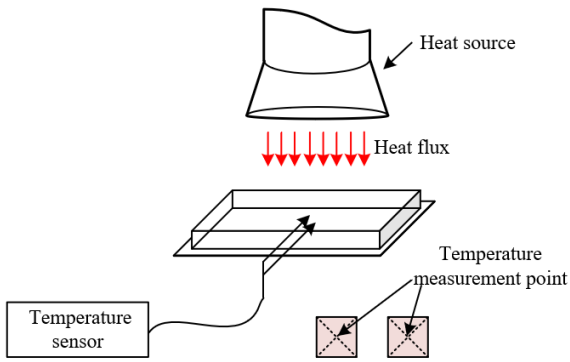


Figure 1. Schematic diagram of the material thermal response experimental setup

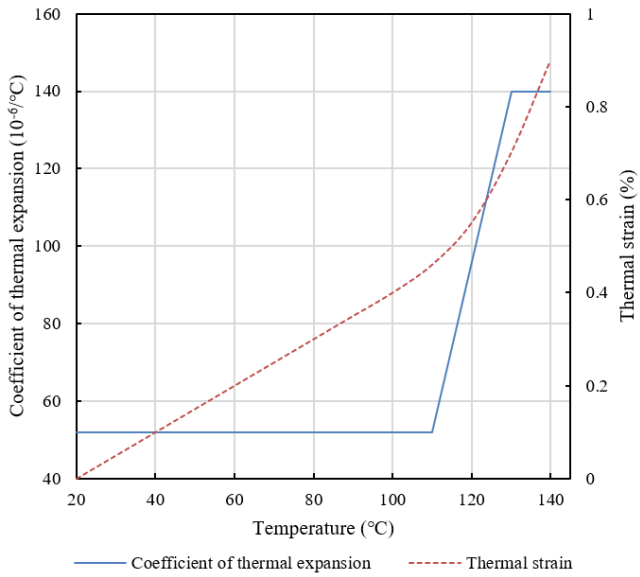


Figure 2. Thermal expansion coefficient of epoxy resin matrix

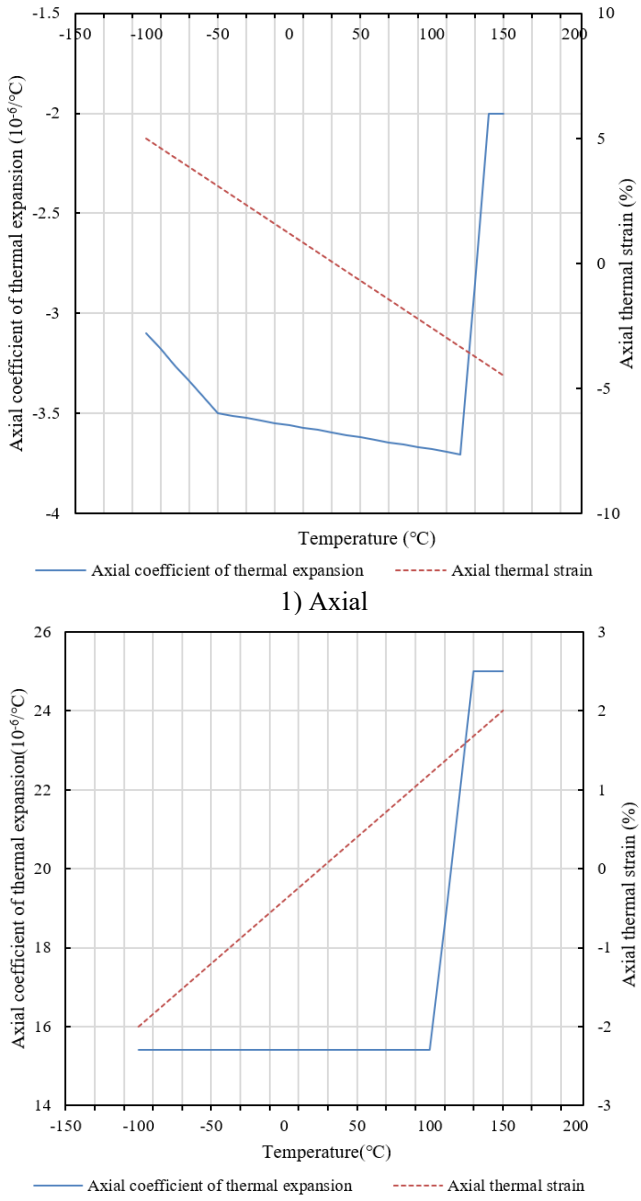


Figure 3. Thermal expansion coefficient of carbon fiber

During the high-temperature curing process, the thermal expansion behavior of the epoxy resin matrix is also influenced by the curing reaction. The temperature change during the curing process causes chemical reactions within the epoxy resin matrix, generating heat and further affecting its volume change. In this process, thermal stresses tend to accumulate within the epoxy resin matrix, especially when a one-step curing method is used. Local thermal stress concentration may lead to fluctuations in the thermal expansion coefficient, which are particularly significant in the glass transition temperature range. Under high-temperature conditions, the release of thermal stress becomes a key issue. In the two-step curing method, the thermal stress accumulation can be effectively alleviated by gradual heating and controlling the curing process, thereby achieving more stable thermal expansion behavior at high temperatures. Therefore, for high-temperature conditions, it is assumed in the model that the thermal expansion coefficient remains stable without fluctuations in the glass transition temperature region and changes linearly, in order to better describe the mechanical properties of the composite material under high-temperature environments. Figure 3 shows the variation of the thermal expansion coefficients of carbon fiber in the axial and transverse directions with temperature.

The thermal expansion behavior of carbon fiber at high temperatures exhibits strong anisotropic characteristics. Carbon fiber, as a high-strength, low-thermal-expansion material, shows significant differences in thermal expansion coefficients in the axial and transverse directions. Typically, the thermal expansion coefficient of carbon fiber in the axial direction is close to zero or negative, while in the transverse direction, it exhibits a positive thermal expansion coefficient. This anisotropic thermal expansion behavior is especially pronounced under high-temperature conditions. As the temperature increases, the negative expansion effect in the axial direction of the carbon fiber may interact with the positive expansion effect in the epoxy resin matrix, leading to significant thermal stress in the interface region of the composite material. Therefore, the model needs to account for the characteristics of the carbon fiber's thermal expansion coefficient as a function of temperature and accurately reflect this thermal expansion difference when calculating the interface thermal stress. To precisely describe the thermal expansion behavior of carbon fiber/epoxy resin matrix composites, assume that β is the thermal expansion coefficient, d, l, and b refer to the fiber, resin, and yarn, respectively, T is the compliance matrix, and U_{jmuk} is the fourth-order symmetric unit tensor. The equivalent thermal expansion coefficient of the composite material can then be calculated based on the Rosen-Hashin theory.

$$\begin{aligned}&\bar{\beta}^b_{uk} = N_d\beta^d_{uk} + (1-N_d)\beta^l_{uk} + \left(\beta^d_{jm} - \beta^l_{jm}\right)\\ &O_{jmlv}\left(\bar{T}^b_{lvuk} - N_d T^b_{lvuk} - (1-N_d)T^l_{lvuk}\right)\\ &O_{jmlv}\left(T^d_{lvuk} - T^l_{lvuk}\right) = U_{jmuk}\end{aligned} \tag{1}$$

The Rosen-Hashin model provides the overall thermal expansion characteristics of composite materials by considering the volume fractions of the fiber and matrix, their respective thermal expansion coefficients, and elastic moduli. Based on this, molecular dynamics simulations can be further used to study the thermal expansion behavior and interface thermal stress of the material at high temperatures. Molecular dynamics simulations can offer a more microscopic analysis of material behavior, particularly under high-temperature conditions, where atomic or molecular interactions will significantly influence the material's thermal expansion characteristics. By precisely simulating the molecular dynamics of carbon fiber and epoxy resin matrix, a more accurate thermal expansion coefficient can be obtained, allowing for the analysis of the thermal stress distribution in the interface region. During the simulation process, intermolecular interaction models at high temperatures, such as the Lennard-Jones potential or EAM model, can be introduced to more accurately describe the thermodynamic behavior of the material under high-temperature conditions.

When studying the thermal expansion properties and interface thermal stress of carbon fiber/epoxy resin matrix composites, the accurate description of interface thermal stress is crucial for understanding the material's mechanical performance in high-temperature environments. The definition of interface thermal stress is based on atomic-level interaction forces in molecular dynamics simulations, particularly changes in interatomic forces in the interface

region. The fundamental cause of thermal stress is the thermal expansion difference caused by temperature changes. When the carbon fiber and epoxy resin matrix have different expansion characteristics under temperature changes, the material at the interface will experience tensile or compressive stress due to this difference. In molecular dynamics simulations, this stress can be quantified by examining the interatomic interaction forces in the interface region. Specifically, temperature changes cause the potential energy between molecules to change, and these changes are manifested as normal and tangential mechanical responses at the contact interface.

In the modeling process of interface thermal stress, it is essential first to consider the impact of the temperature gradient on the interface structure. Since the thermal expansion coefficients of carbon fiber and epoxy resin matrix are significantly different, when the material is exposed to a high-temperature environment, the carbon fiber, due to its low thermal expansion coefficient, will relatively not expand, while the epoxy resin matrix, with its higher thermal expansion coefficient, will exhibit a more significant expansion behavior. As a result, thermal stress induced by the thermal expansion difference will appear at the interface region. These thermal stresses are especially significant under local temperature gradients, so this stress accumulation caused by temperature must be considered in molecular dynamics simulations. To describe the contact relationship between carbon fiber and the resin matrix, a surface bonding model is adopted in this study. This model is defined as a non-coupled linear elastic force-separation relationship. The force and corresponding separation displacement are represented by s and σ, respectively, as shown in the following equation:

$$\begin{Bmatrix} s_1 \\ s_2 \\ s_3 \end{Bmatrix} = \begin{bmatrix} J_{11} & 0 & 0 \\ 0 & J_{22} & 0 \\ 0 & 0 & J_{33} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{Bmatrix} \tag{2}$$

According to this model, the interface contact behavior includes not only the normal contact force but also two tangential contact forces. These contact forces are described through a local coordinate system, where direction 1 represents the normal stress direction, and directions 2 and 3 represent the two tangential stress directions. In this framework, the behavior of the interface is treated as elastic and linear, with contact or separation occurring under external force.

In the assumptions of this chapter's study, interface thermal stress will not cause interface failure. Given the distribution of thermal stress in the interface region under high-temperature conditions, although the thermal expansion coefficient difference between carbon fiber and epoxy resin matrix will generate thermal stress at the interface, the interface will not fail due to bonding under the assumption that the conditions for interface damage are stringent. In other words, despite the presence of thermal stress at the interface, these stresses will not be large enough to cause damage or separation of the interface. Therefore, in the finite element analysis, the interface will be assumed to be in an undamaged state, and all contact forces will remain within the non-coupled linear elastic range. This assumption helps to simplify the complexity of thermal stress analysis while allowing the model to focus on the macroscopic thermal expansion and mechanical behavior of the composite material, without delving into the details of interface damage. It should be noted that although interface failure will not occur, as the temperature increases, the increase in interface thermal stress may affect the performance of the composite material, especially under thermal fatigue and thermal cycling conditions, where the weakening of the interface bonding strength may still influence the final mechanical performance.

3. MOLECULAR DYNAMICS SIMULATION OF MATERIAL INTERFACE THERMODYNAMIC PROPERTIES BASED ON FINITE ELEMENT AND CZM

The thermodynamic properties of composite material interfaces are influenced by the thermal expansion differences between the fibers and resin matrix, the bond strength of the contact interface, and interface stresses, among other factors. In order to capture the interaction between the material's macroscopic mechanical behavior and microscopic structure and to provide a more accurate prediction of interface thermal stresses and mechanical properties, this paper uses finite element and CZM for molecular dynamics simulations of the thermodynamic properties of carbon fiber/epoxy resin matrix composite interfaces. Through mesh refinement, the finite element method can accurately simulate the interface behavior between carbon fibers and the epoxy resin matrix, analyzing the evolution of thermal stresses at the interface at different temperatures, thereby revealing the thermodynamic properties of the interface. The CZM treats the interface as a thin layer region and defines the bond strength, fracture toughness, and other parameters of the interface material by simulating the interface fracture behavior caused by thermal stress, thus characterizing the process of interface fracture or separation.

3.1 Finite element model

When performing molecular dynamics simulations of the thermodynamic properties of carbon fiber/epoxy resin matrix composite interfaces based on finite element and CZM, modeling and computation must be carried out following specific steps. Below are the key steps for simulating the thermodynamic properties of carbon fiber/epoxy resin matrix composite interfaces using the finite element method.

Step 1: Establishment of the Geometric Model

The first step in finite element analysis is to establish an accurate geometric model. In this study, the geometric model dimensions are the same as those of the actual carbon fiber/epoxy resin matrix composite specimen. The accuracy of the constructed model is crucial as it directly affects the reliability of the simulation results and the degree of reproduction of the actual physical phenomena. During the implementation, the geometric model includes the bundle structure of the carbon fibers and the matrix portion of the epoxy resin, and a relatively high-resolution mesh needs to be applied, especially in the interface region, to accurately capture the stress-strain distribution and thermodynamic effects at the interface in subsequent finite element computations. Additionally, the model should consider the size and shape of the actual specimen to ensure that it faithfully reflects the thermodynamic properties of the real material under experimental conditions.

Step 2: Setting the Material Model

Defining the material model, i.e., setting the physical and mechanical properties of the carbon fiber and epoxy resin matrix, is the next step. To accurately simulate the thermodynamic properties of the composite interface, the mechanical properties of the carbon fiber bundles are calculated using the unidirectional plate theory and need to be set according to different directions in the local coordinate system, such as the fiber axial direction and fiber transverse direction. For finite element simulations, parameters such as elastic modulus, Poisson's ratio, and shear modulus in different directions will affect the response characteristics of the interface and the material body. Therefore, selecting and inputting the appropriate material model parameters is the foundation for ensuring the accuracy of the simulation results. Additionally, when considering thermodynamic properties, the material's thermal expansion coefficient, thermal conductivity, and other thermophysical properties should be introduced for effective thermo-mechanical coupling analysis in a multi-physics field scenario.

Step 3: Setting Analysis Steps and Output Variables

The setting of analysis steps determines the operation mode of the finite element simulation and the selection of output variables. Specifically, this study selects appropriate output variables to simulate the mechanical properties and failure modes of the carbon fiber/epoxy resin matrix composite. The outputs in finite element calculations are divided into field variable outputs and history variable outputs. Field variable outputs are used to represent the spatial distribution of variables throughout the material, such as stress, strain, displacement, and applied forces. These variables provide an instantaneous description of the material's state and help identify potential damage regions. History variable outputs are primarily used to track the evolution of variables over time and describe how the material changes during loading, particularly the history of interface damage and crack propagation. In this simulation, the focus is on the mechanical properties of the material and its failure modes, with stress, strain, displacement, and applied force selected as field variable outputs to provide detailed data support for subsequent damage analysis, interface thermodynamic performance evaluation, and crack propagation.

Step 4: Setting Contact Conditions

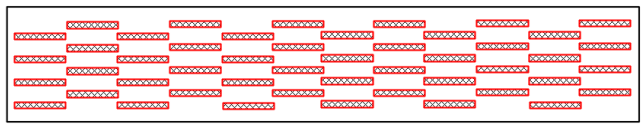
Setting the contact conditions is one of the crucial steps in finite element analysis, especially in interface simulations of composite materials, where accurate simulation of interface behavior directly affects the authenticity and reliability of the calculation results. In this study, the interface between the fiber bundles and the matrix is modeled using cohesive zone properties, simulating a zero-thickness interface that can effectively capture the bonding, slip, and fracture behavior of the interface. In experiments, the movement of the resin matrix is blocked by a steel plate, causing the fiber bundles to detach from the matrix. To avoid sliding between the matrix and the steel plate during loading, the contact condition is set to "Tie contact," meaning no relative displacement exists between the matrix and the steel plate. In this setup, the mesh of the steel plate is coarser, so the surface of the steel plate is defined as the master surface, while the region of the model that contacts the steel plate is defined as the slave surface. This approach ensures that the contact region can effectively transmit mechanical forces under actual loading conditions and avoids numerical instability caused by insufficient mesh refinement.

Step 5: Setting Boundary and Loading Conditions

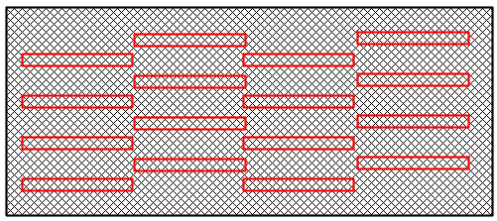
In the high-temperature experimental process, the test machine's lower grip fixes the steel plate, blocking the movement of the epoxy resin matrix. This needs to be constrained in the finite element model. To simplify the problem and ensure that the model accurately simulates the physical phenomena in the experiment, it is assumed that the steel plate will not deform under tensile force, so the steel plate is set as a rigid body. Based on this assumption, all degrees of freedom of the steel plate are constrained, i.e., $I_1 = I_2 = I_3 = IE_1 = IE_2 = IE_3 = 0$, ensuring it remains fixed. At the same time, a displacement load is applied to the free end of the fiber bundles in the model, simulating the tensile process of the fiber bundles in the actual experiment. This boundary and loading condition setup effectively simulates the blocking effect of the steel plate on the matrix movement in the high-temperature experiment and ensures that the fiber bundles generate appropriate stress-strain responses when subjected to tension, providing a reasonable computational foundation for subsequent thermodynamic analysis and failure mode identification.

Step 6: Mesh Partitioning

Mesh partitioning is one of the most critical steps in finite element analysis, as its quality directly determines the accuracy of the simulation results and computational efficiency. In this study, the resin, fiber bundles, and steel plate in the model are meshed using 8-node hexahedral reduced integration elements (C3D8R). Since the focus of the study is on the mechanical performance of the fiber bundles and matrix, the mesh density for the fiber bundles and resin is much higher than that for the steel plate. Specifically, the mesh partitioning in the fiber bundle and resin regions is relatively fine to ensure that local deformations, stress distributions, and failure behaviors during the loading process are captured. For the steel plate, because it only serves as a blocking role and does not directly participate in the material's mechanical response, its mesh partitioning is coarser. This differential mesh partitioning method effectively reduces the overall number of mesh elements, thereby shortening the computation time while ensuring the accuracy of the simulation results. Figure 4 shows the geometric model and mesh partitioning example of the carbon fiber/epoxy resin matrix composite laminate.



1) Geometric model



2) Mesh division

Figure 4. Example of the geometric model and mesh division for the carbon fiber/epoxy resin composite laminate

3.2 CZM model

The molecular dynamics simulation of the thermodynamic properties of the carbon fiber/epoxy resin composite interface based on the CZM can be explained by a detailed analysis of the micro-damage and fracture process of the composite

interface. The core idea of CZM is to describe the fracture process at the microscopic scale, capturing the initiation and propagation mechanisms of cracks. Unlike traditional linear elastic fracture mechanics, CZM avoids the singularity issue at the crack tip by introducing a functional relationship between stress and crack-opening displacement, enabling more realistic simulation of materials under complex stress and temperature fields. Let the stress value be denoted as δ, the crack-opening displacement at the interface as σ, and the interface fracture energy as α. The functional expressions are as follows:

$$\delta = d(\sigma) \tag{3}$$

$$\psi = \int \delta d\sigma = \int f(\sigma) d\sigma \tag{4}$$

In the thermodynamic analysis of the composite material interface, the interface is often subjected to significant thermal stress due to the differences in thermal expansion coefficients between carbon fiber and the epoxy resin matrix. The temperature gradient causes stress to gradually accumulate at the interface, which can potentially trigger the initiation of cracks. The CZM precisely simulates this crack initiation and propagation process by defining the stress-displacement relationship at the interface. According to the basic principle of CZM, the evolution of interface damage can be divided into three stages: initial damage, damage propagation, and complete fracture. During the initial damage stage, the interface stress increases with displacement until it reaches the maximum stress value. At this point, the interface reaches its ultimate bearing capacity, and damage begins to initiate. During the damage propagation stage, the crack continues to grow, and the material stress decreases until complete failure occurs.

In the molecular dynamics simulation of the thermodynamic properties of the carbon fiber/epoxy resin composite interface based on CZM, the initiation of initial damage usually relies on certain damage criteria. These criteria are used to determine when the interface material begins to experience damage and initiate the crack initiation and propagation process. ABAQUS software provides four common initial damage judgment criteria: maximum stress criterion, quadratic stress criterion, maximum strain criterion, and quadratic strain criterion.

The maximum stress criterion assumes that when the internal stress of the material exceeds a certain threshold value, initial damage will occur at the interface. This threshold stress is usually based on experimental or empirical data. For carbon fiber/epoxy resin composites, this criterion is suitable for damage judgment when the interface is subjected to localized high stress. Due to the differences in elastic modulus and thermal expansion coefficient between carbon fiber and the epoxy resin matrix, the interface may experience high stress, especially under large temperature gradients. Using the maximum stress criterion, interface damage occurs when the material's internal stress exceeds a critical value and then propagates into crack growth. In the molecular dynamics simulation, by tracking the stress state between atoms at the interface, regions where stress exceeds the critical value can be precisely identified, and the damage mechanism in the CZM is activated to simulate the crack initiation and propagation process. The specific expression is as follows:

$$MAX\left\{\frac{\langle \delta_v \rangle}{\delta_v^{MAX}}, \frac{\delta_t}{\delta_t^{MAX}}, \frac{\delta_s}{\delta_s^{MAX}}\right\} = 1 \tag{5}$$

The quadratic stress criterion determines damage occurrence by combining the stress components quadratically. Compared to the maximum stress criterion, the quadratic stress criterion considers the damage behavior of materials under multi-axial stress states. In composite interfaces, multi-directional stress interactions often exist, especially under temperature changes or external loads. Therefore, the quadratic stress criterion can more accurately describe the damage behavior of composite interfaces under complex stress fields. In molecular dynamics simulation, the quadratic stress criterion can be used to analyze stress in different directions, identify the initiation points of damage under multi-directional stress, and provide more precise simulation support for crack initiation and propagation. The specific expression is:

$$\left\{\frac{\langle \delta_v \rangle}{\delta_v^{MAX}}\right\}^2 + \left\{\frac{\delta_t}{\delta_t^{MAX}}\right\}^2 + \left\{\frac{\delta_s}{\delta_s^{MAX}}\right\}^2 = 1 \tag{6}$$

The maximum stress criterion posits that when the local strain of the material exceeds a certain threshold value, initial damage will occur at the interface. In carbon fiber/epoxy resin composites, due to the differences in thermal expansion coefficients, the temperature gradient can cause significant strain at the interface, especially in high-temperature environments where accumulated thermal strain can lead to interface damage. The maximum strain criterion is suitable for strain-dominated damage processes, such as interface deformation caused by thermal expansion mismatch. When the strain in a unit at the interface exceeds the critical value, initial damage is triggered, and cracks initiate and propagate. By combining molecular dynamics simulation, the maximum strain criterion can precisely calculate the strain at the interface, simulate the strain concentration regions caused by temperature changes, and provide detailed information on the damage initiation points and crack propagation. The specific expression is:

$$MAX\left\{\frac{\langle \sigma_v \rangle}{\sigma_v^0}, \frac{\sigma_t}{\sigma_t^0}, \frac{\sigma_s}{\sigma_s^0}\right\} = 1 \tag{7}$$

The quadratic strain criterion is similar to the quadratic stress criterion, it uses the quadratic combination of strain components to determine damage occurrence. This criterion is applicable to interfaces with complex strain distributions and multi-directional strain interactions. In carbon fiber/epoxy resin composites, the interface is typically subjected to coupled strains in different directions, especially under multi-axial loads and temperature gradients. The quadratic strain criterion can more comprehensively reflect the damage behavior of interfaces under these complex conditions. In molecular dynamics simulation, the quadratic strain criterion can capture strain accumulation in different directions at the interface through fine atomic-scale strain analysis, simulating the early stages of interface damage and guiding the crack propagation process. Assuming the normal and two shear directions are denoted by v, t, and s, and the maximum stress and corresponding interface opening displacement are denoted by δ^{MAX} and δ^0, the specific expressions are as follows:

$$\left\{\frac{\langle\sigma_v\rangle}{\sigma_v^0}\right\}^2+\left\{\frac{\sigma_t}{\sigma_t^0}\right\}^2+\left\{\frac{\sigma_s}{\sigma_s^0}\right\}^2=1 \tag{8}$$

$$\langle\delta_v\rangle=\begin{Bmatrix}0 \Leftarrow \delta_v \le 0\\ \delta_v \Leftarrow \delta_v > 0\end{Bmatrix} \tag{9}$$

$$\langle\sigma_v\rangle=\begin{Bmatrix}0 \Leftarrow \sigma_v \le 0\\ \sigma_v \Leftarrow \sigma_v > 0\end{Bmatrix} \tag{10}$$

In molecular dynamics simulations, the application of CZM generally relies on the cohesive law, which is used to describe the damage evolution of interface materials. The bilinear model selected in this study describes the entire process from initial damage to crack propagation. Let the opening displacement at the unit node at the initiation of failure be denoted as σ^0, the opening displacement at complete failure be denoted as σ^d, and the maximum opening displacement during the load history be denoted as σ^{MAX}. The calculation formula is as follows:

$$F=\frac{\sigma^d\left(\sigma^{MAX}-\sigma^0\right)}{\sigma^{MAX}\left(\sigma^d-\sigma^0\right)} \tag{11}$$

Specifically, in the bilinear model, as the crack opening displacement increases, the stress initially increases until it reaches a maximum value, at which point the material enters the initial damage stage. Afterward, the stress begins to decrease until complete failure occurs. The process of stress decrease is represented by a stiffness degradation factor F, where the value of F ranges from 0 to 1, with F = 0 indicating intact material and F = 1 indicating complete failure of the material. During this process, the stiffness of the material weakens as damage evolves, which impacts the interface's mechanical performance and thermodynamic response.

The application of the bilinear model allows us to accurately capture the evolution characteristics of interface damage between carbon fiber and epoxy resin matrix under different temperature conditions. Especially when the material is affected by thermal stress, micro-cracks may appear at the interface due to the difference in thermal expansion coefficients between carbon fiber and the epoxy resin matrix. In molecular dynamics simulations, by combining CZM and the bilinear model, we can track the atomic interactions at the interface, capturing the initiation and propagation of cracks in real-time and precisely simulating the mechanical response of the interface material based on the relationship between stress and displacement. This process provides detailed micro-mechanical analysis of composite material behavior under thermal load and serves as a theoretical basis for designing high-performance composite materials.

4. EXPERIMENTAL RESULTS AND ANALYSIS

To further verify the consistency between the simulation results and actual experimental data, we analyzed the temperature field distribution of carbon fiber/epoxy resin-based laminates under different temperature conditions in the experimental section. In the temperature field distribution chart, although the temperature change trends are consistent, due to the small thickness of the carbon fiber and its good thermal conductivity, its temperature change is relatively smooth, and the temperature rise rate of carbon fiber is slower than that of the epoxy resin matrix (Figure 5). This means that in the initial stage of material exposure to heat, the temperature difference between the carbon fiber and the epoxy resin matrix is small. As time progresses, the temperature gradient gradually intensifies, especially under sustained heat flux, the temperature difference at the interface will increase, causing thermal stresses to accumulate at the interface.

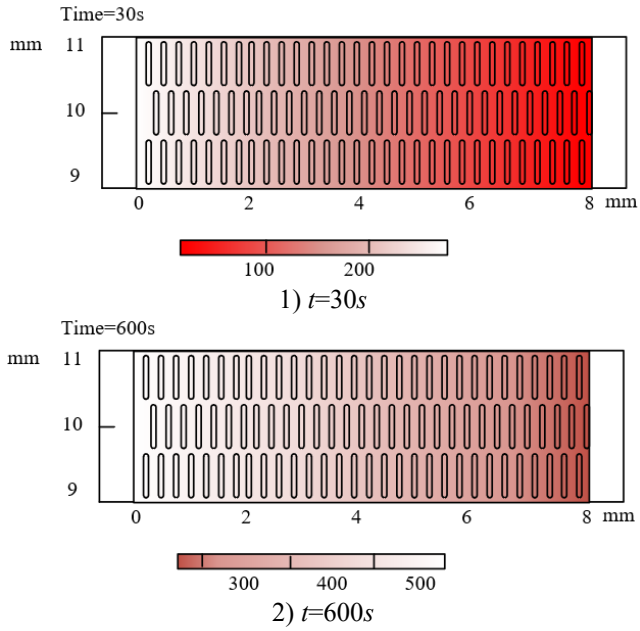


Figure 5. Temperature distribution of carbon fiber/epoxy resin-based composite specimens at different time intervals under different temperature environments

From the perspective of combining simulation and experimental data, although the temperature difference between carbon fiber and epoxy resin matrix is relatively weak, it still has a significant impact on the thermal stress at the interface. Especially at the interface, thermal expansion mismatch may lead to localized thermal stress concentration. As molecular dynamics simulation can capture thermodynamic behaviors at the microscopic scale, it can precisely reveal the distribution of thermal stress at the composite material interface. In this study, the molecular dynamics simulation results show that the distribution of thermal stress in the interface region is closely related to the temperature gradient. As the temperature gradually rises, the thermal stress in the interface region increases, potentially leading to interface delamination or other forms of failure.

The results in Figure 6 further verify the thermodynamic response mechanism simulated, particularly in terms of the thermal stress and morphological changes of the composite material under heat treatment conditions. The experimental results show that before heat treatment, the height difference between the resin and fiber marker points is significantly smaller than after heat treatment, especially in the resin region where shrinkage is particularly noticeable. This phenomenon is closely related to the further curing of the resin during the heat treatment process. Such shrinkage behavior directly reflects the thermal expansion difference between the resin and carbon fiber and the changes in interface thermal stress.

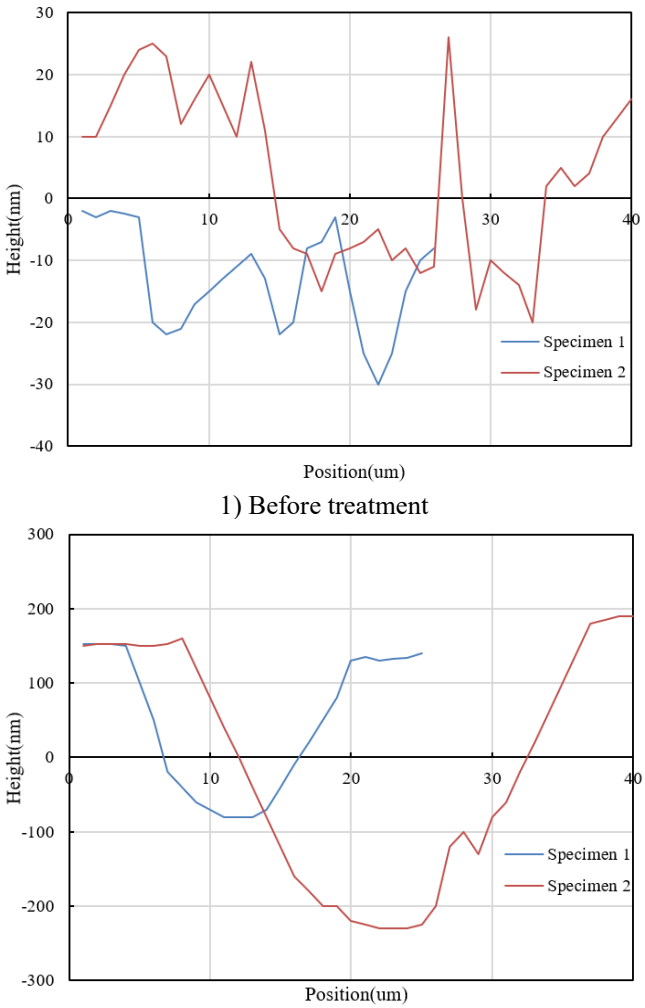


Figure 6. The effect of heat treatment on the microstructure of carbon fiber/epoxy resin-based composite specimens

According to the experimental data, in the initial morphology before heat treatment, the morphology changes between two marker points were 13 nm and 14 nm, indicating a small material size change, mainly due to weak thermal expansion effects. However, after heat treatment, the morphology change between the two marker points increased significantly to 240 nm and 360 nm, respectively (Figure 7). This change reflects the significant shrinkage behavior of the resin during heat treatment. The epoxy resin matrix undergoes further curing under heating conditions, which not only increases the volume shrinkage of the resin but also possibly leads to an increase in interface stress between the resin and the fiber. As carbon fiber has a smaller thermal expansion coefficient compared to the epoxy resin matrix, the shrinkage of the resin during heat treatment will inevitably cause thermal stress concentration at the interface, especially when the fiber spacing is large, the resin shrinkage is more pronounced.

Furthermore, we employed a fine measurement method by selecting any two adjacent carbon fibers on the sample and using the shortest connecting line between the fibers as the object of study to quantify the thermal expansion effects of the composite material and the shrinkage of the resin during the heat treatment process. Before heat treatment, the initial geometry of the region was represented by A1 and B1, which were the intersections of the shortest connecting line between the fibers and their cross-sectional areas. After heat treatment, we measured the change in the same shortest connecting line and intersection positions, designated as A2 and B2. This change is defined as the horizontal distance change ΔA between the fibers and the shrinkage of the resin ΔB. With this method, we systematically tracked the interaction between resin shrinkage and the fibers, analyzing how thermal expansion and interface thermal stress affect the material's properties.

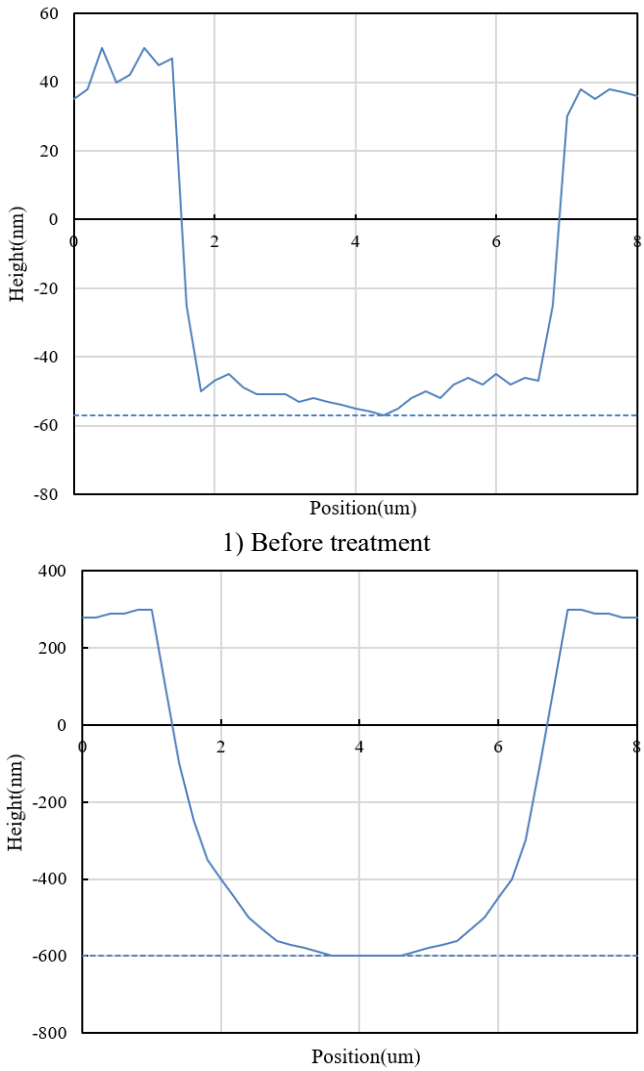


Figure 7. Microstructure of the carbon fiber/epoxy resin-based composite specimen and related parameters

According to the experimental results, as heat treatment progresses, we observed a significant change in the average horizontal distance ΔA between adjacent fibers. This change is not merely due to the thermal expansion of the carbon fiber, but more as a result of the resin curing and shrinking during the heat treatment process. Especially at higher temperatures, the resin's curing process is significantly intensified, causing the shrinkage of the resin to further increase the amplitude of ΔB. Under different heat treatment conditions, we also found that there was a certain correlation between fiber spacing and resin shrinkage amplitude, indicating that the fiber-resin bonding performance under heat treatment is greatly influenced by temperature and the degree of resin curing.

To further analyze the effect of heat treatment on the fiber-resin interface bonding strength, we compared the ΔA and ΔB

values at different positions, revealing the unique impact of wet-heat treatment on the interface structure. Under wet-heat treatment conditions, the relationship between fiber spacing ΔA and resin shrinkage amplitude ΔB exhibited significant non-linear changes, especially in high-temperature and high-humidity environments where the resin shrinkage amplitude increased more significantly, while the fiber spacing change was limited by the resin's curing characteristics. This phenomenon indicates that the bonding strength between the resin and carbon fiber is affected by temperature, humidity, and the resin's curing state, and the wet-heat treatment environment may lead to a decrease in the bonding strength at the interface, thus affecting the overall mechanical properties of the composite material.

By combining these experimental observations with molecular dynamics simulation results, we can further explain these findings at the microscopic scale. The simulation indicates that as the temperature rises, the thermal stress at the carbon fiber and epoxy resin matrix interface gradually increases, especially as thermal expansion mismatch becomes more apparent during the resin curing process. The resin shrinkage leads to stress concentration at the interface, which may cause interface failure or delamination. Especially under wet-heat conditions, the resin's adhesive properties may be affected by both temperature and humidity, causing changes in the molecular chain structure of the resin, thereby weakening its bonding strength with the fibers (Figure 8).

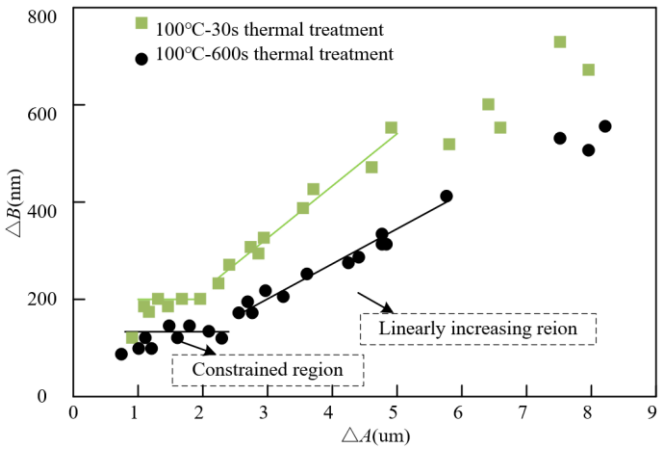


Figure 8. The relationship between the average horizontal distance ΔA of the carbon fiber/epoxy resin matrix composite sample treated at 100°C for 30s and 600s, and the resin shrinkage ΔB

The experimental section further reveals the interface response mechanism of the composite material during the heat treatment process by measuring the horizontal distance ΔA between adjacent fibers and the shrinkage amplitude ΔB of the resin between the fibers. The experimental results show that when the average horizontal distance ΔA between adjacent fibers is less than about 1.8 μm, the resin shrinkage amplitude ΔB is small and stable, indicating that within this fiber spacing range, the thermal expansion behavior of the resin is effectively constrained by the fibers. As the fiber spacing increases, the resin shrinkage amplitude ΔB gradually increases and exhibits a distinct nonlinear variation trend. Particularly when the fiber spacing exceeds 5.0 μm, the increase in resin shrinkage amplitude no longer follows a linear pattern and may be influenced by the interaction with other adjacent fibers.

To further analyze this phenomenon, we performed linear fitting on the data of fiber spacing ΔA within the range of 2.0 μm to 5.0 μm, and obtained the corresponding fitting formula and variance. The appearance of this linear relationship suggests that within this fiber spacing range, the thermal expansion behavior of the resin is mainly limited by the mutual constraint forces between the fibers, and the increase in fiber spacing directly leads to an increase in resin shrinkage amplitude. However, when the fiber spacing increases further, especially beyond 5.0 μm, the interaction forces between fibers are no longer solely confined to the immediate neighboring fibers, and may be affected by other neighboring fibers, making the resin shrinkage behavior more complex and causing the relationship between ΔB and ΔA to no longer show a clear linear variation.

The mechanism behind this phenomenon can be further explained through molecular dynamics simulation. At the microscopic scale, the interaction forces and thermal expansion behavior between the resin and carbon fiber are influenced by the fiber spacing and the interface bonding strength. The high rigidity and low thermal expansion coefficient of carbon fibers restrain the resin's shrinkage during heat treatment, particularly when the fiber spacing is small, the thermal expansion behavior of the resin is effectively restricted, leading to a smaller shrinkage amplitude ΔB. As the fiber spacing increases, the shrinkage amplitude of the resin gradually increases because the restraining effect between the fibers weakens, and the freedom of the resin molecular chains increases, making its thermal expansion behavior more noticeable.

When the fiber spacing exceeds 5.0 μm, the increase in resin shrinkage amplitude no longer follows a simple linear relationship, which may be related to the microstructure of the composite material and the interactions between adjacent fibers. When the fiber spacing is large, the resin shrinkage is not only constrained by the adjacent fibers but also affected by more microscopic structural factors. For instance, there may be irregularities in the fiber arrangement, interfacial effects between the fiber and resin, and the arrangement and orientation of the fibers, which contribute to the complexity of the resin shrinkage behavior and thus affect the relationship between ΔB and ΔA.

The molecular dynamics simulation results can further verify this hypothesis. The simulation shows that when the fiber spacing is small, the interaction force between the resin and fiber interface is strong, which restricts the resin's thermal expansion behavior, leading to a smaller shrinkage amplitude. As the fiber spacing increases, the freedom of the resin molecular chains increases, resulting in a larger resin shrinkage amplitude. Additionally, due to the weakening of the interaction force between fibers, the distribution of thermal stress at the interface also changes. Particularly when the fiber spacing exceeds 5.0 μm, the distribution of thermal stress becomes more complex, and stress concentration phenomena may occur, leading to failure of the interface layer.

5. CONCLUSION

This paper combined molecular dynamics simulation and experimental methods to study the interfacial thermodynamic properties of carbon fiber/epoxy resin matrix composites, focusing particularly on the thermal expansion behavior and evolution of interfacial thermal stresses under heat treatment

conditions. The core of the study is to reveal the interface response mechanism between carbon fiber and epoxy resin matrix, analyze the distribution of interfacial thermal stresses and thermal expansion effects under different heat treatment conditions, and further explore the impact of these changes on the composite material's performance. Through multiscale simulation methods, including molecular dynamics simulation and finite element analysis, we are able to systematically study the thermodynamic properties and failure behaviors of the material at both the microscopic and macroscopic scales.

This study, by combining molecular dynamics simulations with experimental methods, provides an in-depth exploration of the interfacial thermodynamic properties of carbon fiber/epoxy resin matrix composites during heat treatment. Specifically, this study reveals the thermal expansion differences between the fibers and resin, the distribution of interfacial thermal stresses, and the impact of heat treatment on interfacial failure behaviors. These findings provide important theoretical insights for understanding the thermal failure mechanisms and interface behavior of composite materials. These results are significant not only for optimizing the design of composite materials and improving their thermal stability and mechanical performance but also for providing valuable guidance for the application of composite materials in high-temperature environments.

Although this study has deeply analyzed the interfacial thermodynamic properties using molecular dynamics simulations and experimental methods, there are still certain limitations. First, molecular dynamics simulations are typically limited by smaller computational scales and simulation times and cannot comprehensively cover the thermodynamic responses of large-scale composite material structures. Second, this study primarily focuses on specific experimental conditions and does not consider other factors that may affect interfacial thermodynamic properties, such as different resin formulations, fiber surface treatments, or external loads. Additionally, the impact of humid heat conditions has not been systematically simulated and experimentally studied, and the specific effects of moisture on the resin molecular chain structure need further investigation.

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