

Key Physicochemical Properties and Service Characteristics of Low Dielectric Polyimide-based Nanocomposites

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Abstract In high-frequency electrical energy systems, polyimide (PI) composite insulation materials need to possess a low dielectric constant, sufficient thermal conductivity, and robust interfacial adhesion to ensure reliable performance under elevated temperatures and pressures. These aspects are crucial for preventing local overheating and electrical breakdown, thereby ensuring reliable equipment operation. Traditional PI insulation materials often exhibit high dielectric constants and pronounced dielectric losses, compromising their insulation efficiency. In this study, molecular dynamics simulations were employed to incorporate polyhedral oligomeric silsesquioxanes (POSS) into PI through physical blending and chemical bonding to enhance dielectric properties. Key parameters of the PI/POSS composite system, including dielectric constant, thermal conductivity, glass transition temperature, Young's modulus, Poisson's ratio, and interfacial adhesion energy, were systematically evaluated for both doping methods. The degradation behavior of the PI composites under high-temperature and electric field conditions was also simulated to elucidate degradation pathways and product distributions, providing insights for designing low-dielectric insulation materials. Doping with POSS significantly reduces the dielectric constant of PI, thereby improving insulation performance, thermal stability, mechanical strength, and interfacial adhesion. At an optimal POSS doping ratio, the thermal conductivity of PI is enhanced. Compared with the physical blending system, the chemical bonding system yields more substantial improvements across all evaluated properties. Under high-temperature and strong electric field conditions, POSS doping enhances interfacial adhesion and thermal stability, effectively suppressing the cleavage of key chemical bonds, reducing CO emissions, and increasing the formation of oxygen-containing intermediates and water molecules, which contributes to improved environmental sustainability.

Keywords Polyimide; Molecular dynamics simulation; Dielectric constant; Thermal conductivity; Electrothermal aging

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INTRODUCTION

Polyimide (PI), with its unique imide ring structure, exhibits excellent mechanical properties, a wide temperature applicability range, outstanding insulation characteristics, and good chemical stability.^[1] Owing to its exceptional physical and chemical properties, PI has considerable application potential in various fields, such as electrical engineering, defense, electronic communication, and aerospace, but the performance requirements in these areas are becoming increasingly stringent.^[2,3]

For example, with the development of high-frequency power transformers, insulation materials must withstand extreme conditions such as high frequency and high temperature. However, due to its high dielectric constant and decreased thermal stability, traditional PI struggles to meet the insulation demands of the equipment, significantly impacting the reliability and lifespan of the materials. Therefore, enhancing the thermal stability of PI to adapt to high-tempera-

ture environments is essential. Additionally, strong mechanical properties are crucial for the structural stability and durability of power transformers. Although PI possesses high tensile strength, the mechanical performance of the material may deteriorate under high pressure and strong electric fields.

In light of these challenges, the trade-off among the dielectric loss, thermal resistance, and mechanical strength is extremely important when the PI performance is enhanced. While reducing the dielectric constant helps to decrease dielectric loss, this may alter the molecular structure of the material and subsequently affect its thermal stability. Thus, both aspects need to be considered during the optimization process. Furthermore, increasing the mechanical strength may lead to a decrease in the dielectric performance; research shows that certain reinforcing agents can induce defects while increasing the strength, thereby increasing the dielectric loss. Therefore, achieving an optimal balance among the dielectric performance, thermal properties, and mechanical properties of the material is a key challenge in improving the application of PI in high-frequency power transformers.

In recent years, numerous studies have shown that meth-

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ods to reduce the dielectric constant of PI mainly include the introduction of the fluorine-containing groups, the incorporation of alicyclic structures, and the preparation of porous PI.^[4–12] Regarding the introduction of the fluorine-containing groups, C.D. Simone *et al.*^[13] synthesized a series of pendant perfluorinated aromatic PIs (8F-PIs) that exhibited a lower dielectric constant. In an approach involving alicyclic structures, Ririka *et al.*^[14] prepared seven types of PI (ISS-PI) through the reaction of isosorbide dianhydride (ISS-DA) with different diamines; these structures possessed dielectric constants in the approximate range of 2.97 to 3.33. For the preparation of porous PI, Cui Xue *et al.*^[15] used a hard template method to create hollow meso-porous SiO₂ nano-microspheres; these nano-microspheres significantly enhanced the hydrophobicity and dielectric performance of the PI films, and the minimum dielectric constant was reduced to 2.80. To improve the thermal conductivity of PI, Wu Zhiqiang *et al.*^[16] constructed PI/reduced graphene oxide and boron nitride nanosheet composites with a core-shell structure, and these composites significantly increased the out-of-plane thermal conductivity and effectively met the heat dissipation needs of advanced electronic devices. Wang Ting *et al.*^[17] prepared boron nitride nanosheets (BNNs) using a melt-hydroxide-assisted liquid exfoliation method and introduced them as fillers into the PI composite films; these films showed an increase in the in-plane thermal conductivity of up to 1080% with respect to that of pure PI.

In summary, although significant progress has been made in previous studies to reduce the dielectric constant and enhance the thermal conductivity of the PI-based composites, PI composite insulation materials still face considerable challenges in the application of high-frequency power transformers. First, in addition to having a low dielectric constant, the composites need to also possess appropriate thermal conductivity and excellent interfacial adhesion energy to ensure stable insulation performance under high-temperature and high-pressure conditions; composites with these characteristics can prevent local overheating and electrical breakdown and ensure the reliable operation of the equipment. Second, the glass transition temperature of the PI composites is an important indicator for assessing their high-temperature resistance, and Poisson's ratio and Young's modulus are crucial parameters for evaluating their mechanical properties. Notably, trade-off often exists between improving the dielectric performance, thermal conductivity, and mechanical strength of PI. Additionally, the degradation of PI in high-temperature and strong electric field environments can lead to material failure; thus, an examination of the mechanisms and decomposition pathways can aid in the development of new composite materials that are more resistant to high temperatures and strong electric fields.

Therefore, although some studies have improved the dielectric or thermal properties of PI insulation composites through physical or chemical methods, there is still insufficient comprehensive evaluation and analysis of the trade-offs among the dielectric constant, thermal conductivity, interfacial adhesion energy, glass transition temperature, Poisson's ratio, and Young's modulus of PI composites, along with an in-depth investigation of their degradation mechanisms un-

der high temperatures and strong electric fields. For this reason, conducting a more systematic and in-depth study of PI composites is highly important.

Polyhedral oligomeric silsesquioxane (POSS) is an organic-inorganic hybrid molecule with a nanocage structure; thus, it is an ideal material for incorporation into PI films. The unique silicon-oxygen inorganic core of POSS is surrounded by organic groups to ensure good compatibility with polymers; this effectively prevents agglomeration and ensures material uniformity and stability. Moreover, due to its excellent oxidative resistance and thermal stability, POSS can maintain polymer performance at high temperatures. Additionally, its uniform nanoscale pores can effectively reduce the dielectric constant of composite materials without compromising their mechanical properties. Moreover, combining PI with fillers and introducing nanoporous or mesoporous structures is an effective method for enhancing PI performance.^[18–20] With the advancement of nanotechnology, POSS-based PI/POSS insulating composite materials have become popular in dielectric material research.

The two main preparation methods for introducing POSS into PI are physical blending and chemical bonding. The physical blending method involves directly mixing POSS with PI and is simple and quick to perform; however, a high doping ratio may lead to agglomeration, thereby affecting the material's performance. The chemical bonding method connects POSS with PI macromolecules through covalent bonds; this process allows the POSS molecules to integrate deeply into the PI molecular network and create more robust bonds.

In recent years, advancements in molecular dynamics simulation technology have facilitated new opportunities for scientific research and have led to revolutionary changes in various fields, including chemical engineering, pharmaceuticals, and new materials.^[21–26] This technology enables the study of system evolution and macroscopic properties at the atomic level, can be used to predict the material properties, and significantly reduces R&D costs and time. In this study, molecular dynamics simulation is utilized to overcome the limitations of traditional experimental methods in terms of cost and time, achieving a comprehensive investigation of the performance of the PI/POSS composite system. This method is used to examine the electrothermal aging mechanisms and degradation pathways of the composite system in depth and can be used to compare the material performance under two preparation methods (physical blending and chemical bonding) to assess the impact of the different doping methods on the overall performance of the materials. This provides an important theoretical foundation and experimental guidance for future material design and optimization.

In this study, molecular dynamics simulation is used to construct a pure PI system, and POSS is combined with different mass fractions of PI using both physical blending and chemical bonding to form PI/POSS composite systems. The impacts of the two doping methods on the key properties of the composite materials (dielectric constant, thermal conductivity, interfacial adhesion energy, Poisson's ratio, Young's modulus, and glass transition temperature) are systematically compared, and their microscopic structure and dynamic behavior under various temperatures, pressures, and strain conditions

are evaluated. Additionally, the degradation process of the PI/POSS composite system under high-temperature and strong electric fields is simulated, and the mechanisms of electrothermal aging and microscopic degradation are revealed. In this study, for the first time, a systematic comparison of the comprehensive performance of physical blending and chemical bonding is presented, and the relationship between the structure and performance of composite materials is examined to provide a theoretical basis and design guidance for developing new PI/POSS composites that are resistant to high temperatures and strong electric fields. It also proposes new concepts for optimizing their design in harsh application environments, such as high-frequency power transformers.

METHODOLOGY FOR PERFORMANCE ANALYSIS OF PI/POSS COMPOSITES AND STUDY OF DEGRADATION MECHANISMS UNDER HIGH TEMPERATURE AND ELECTRIC FIELDS BASED ON MOLECULAR DYNAMICS

Molecular Dynamics Simulation Method

Molecular simulation is a method used to study the behavior of molecular systems under different conditions. This method simulates the interactions between the atoms and molecules using numerical calculations to predict their structures, dynamics, and properties under specific conditions. Molecular simulation is generally based on Newton's laws of motion and quantum mechanics and enables the investigation of the behavior of atoms and molecules at various temperatures, pressures, and chemical environments, thus providing important information on the properties of the system. Molecular dynamics (MD) simulation is a commonly used approach in molecular simulations that simulates the dynamic behavior of a system by solving Newton's equations of motion and is typically utilized to study the structure and dynamic behavior of the system. The following are several key principles and formulas of molecular dynamics simulation.

In molecular dynamics simulations, potential energy functions are typically employed to calculate the interaction potential energy between molecules.

Lennard–Jones Potential is defined as follows:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where ε is the depth of the potential well; σ is the effective diameter of the particles; and r is the distance between the particles.

Coulombic potential (for charged particles) is defined as follows:

$$V(r) = \frac{k \times q_1 \times q_2}{r} \quad (2)$$

where k is Coulomb's constant and q_1 and q_2 are the charges of the two charged particles.

In MD simulations, the forces acting on microparticles (such as atomic nuclei) during their motion are determined by Newton's equations, specifically the relationship between the forces and their potential energy as well as their positions, given by the following formula:

$$\mathbf{F}_i = -\nabla_{\mathbf{n}_i} U(\mathbf{n}) \equiv -\frac{\partial U(\mathbf{n})}{\partial \mathbf{n}_i} = -\left\{ \frac{\partial U}{\partial x_i} \mathbf{i} + \frac{\partial U}{\partial y_i} \mathbf{j} + \frac{\partial U}{\partial z_i} \mathbf{k} \right\} \quad (3)$$

where $\mathbf{F}_i$, $U(\mathbf{n})$, and $\mathbf{n}_i$ represent the force acting on the i^{th} atomic nucleus, the induced potential energy, and the gradient of the induced potential energy relative to the atomic positions, respectively.

By repeatedly calculating the forces and updating the positions and velocities using Newton's second law and the above formulas, the behavior and evolution of the molecular system under specified conditions can be simulated. Molecular dynamics simulations have been widely applied in various fields, such as materials science, biophysics, and chemistry, to predict and understand the interactions between molecules. In this study, molecular dynamics simulation methods are used in conjunction with the Amsterdam Modeling Suite, LAMMPS, and Materials Studio software to conduct an in-depth investigation of the PI/POSS composite system. By leveraging the synergistic effect of these software tools in conjunction with a series of calculations and analyses, the structure, performance, and interactions of the composite system are comprehensively analyzed, leading to a deeper understanding of the characteristics of the PI/POSS composites and their behavior under different conditions, as illustrated in the simulation flowchart in Fig. 1.

Model Construction and Energy Optimization of the PI/POSS Nanocomposites

In this study, three models for synthesizing PI composite systems were initially constructed: the PI repeating unit model, phenyl monofunctional POSS, and aminopropyl-phenyl bifunctional POSS. After performing geometric optimization on each monomer model, the PI molecular chain model and the PI molecular chain model containing POSS were constructed, as shown in Fig. 2. In the PI composite system constructed using the chemical bonding method, the amino hydrogen atoms at both ends of the aminopropyl-phenyl POSS side chains were set as terminal atoms and bonded to the hydrogen atoms at both ends of the PI repeating units, forming a PI molecular chain model containing POSS. To avoid interference between the terminal molecular chains, a simplified polymer structure with a degree of polymerization of 4 was chosen to facilitate modeling and simulation while also reducing computational costs and errors.

The PMDA-ODA type polyimide was selected as the model structure because it is widely used in high-frequency electrical energy systems, such as power transformers, due to its excellent thermal stability and mechanical properties, aligning with our focus on improving insulation performance under high-temperature and high-pressure conditions. Furthermore, its well-characterized molecular architecture and extensively validated force field parameters in the COMPASS force field ensure the accuracy of our MD simulations. The PMDA-ODA structure also serves as a representative benchmark, frequently studied in similar applications.^[1]

The constructed molecular chain models exhibited high energy levels and instability; therefore, geometric optimization needed to be performed on the polymer molecular chains to achieve a stable state, followed by the construction of periodic structures. In the chemical bonding system, the mass fraction of POSS was controlled by varying the propor-

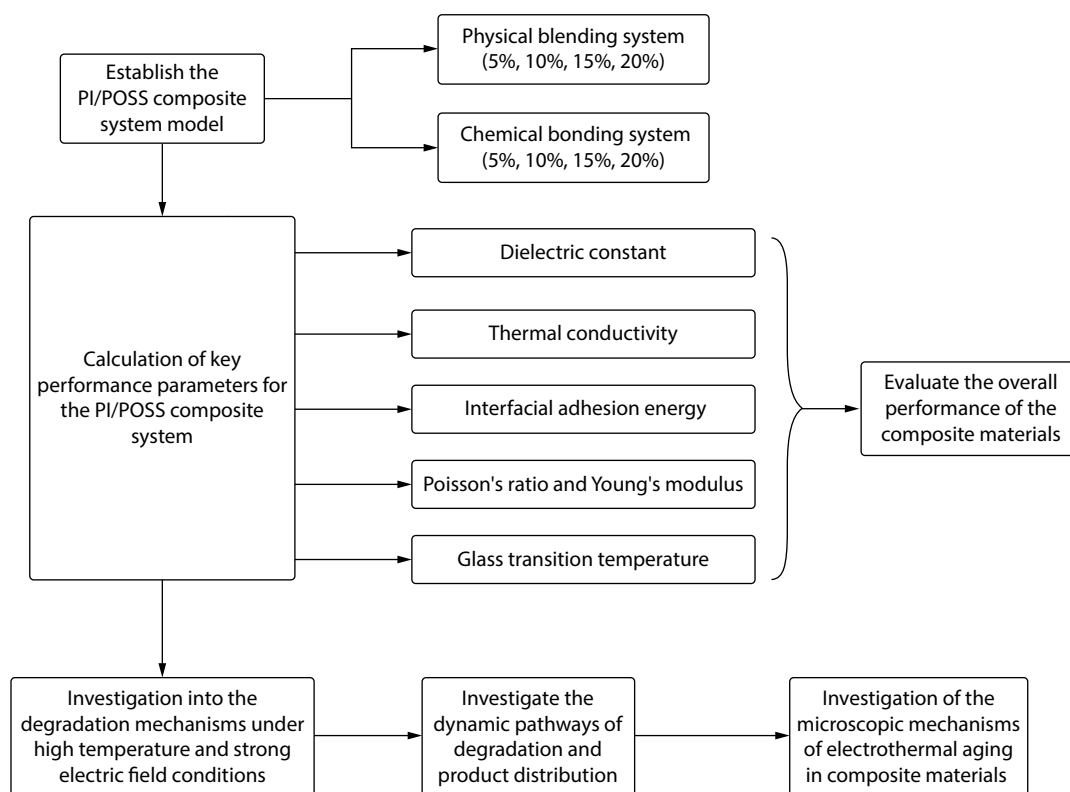


Fig. 1 Simulation flowchart.

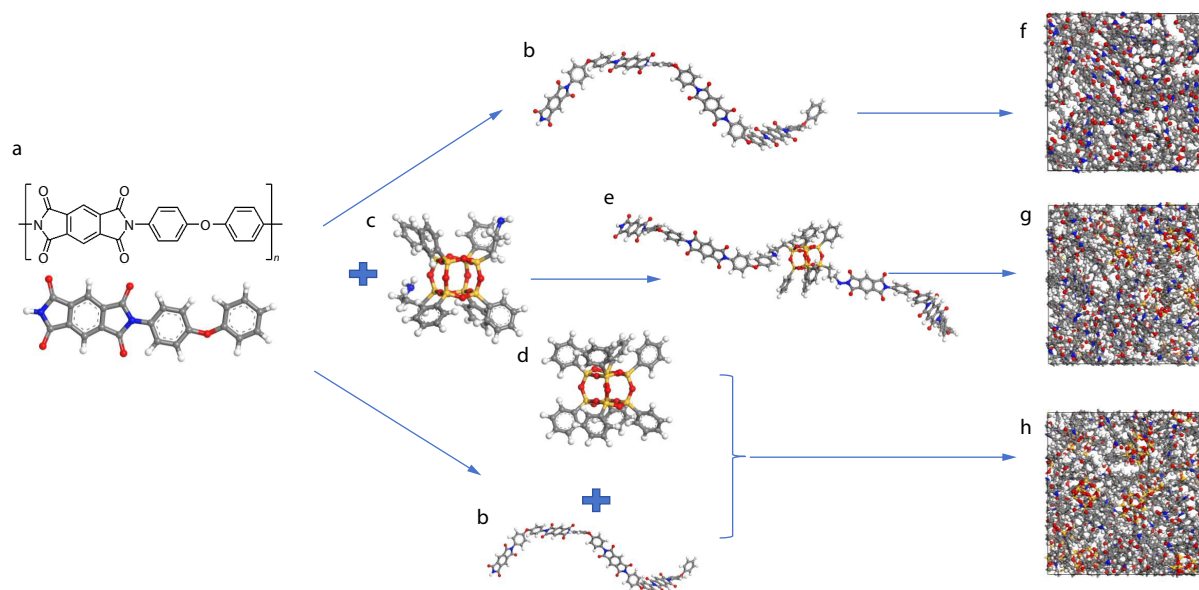


Fig. 2 Model construction diagram: (a) structure of PI repeating unit; (b) pure PI molecular chain; (c) structure of aminopropyl-phenyl bifunctional POSS; (d) structure of phenyl monofunctional POSS; (e) PI molecular chain containing aminopropyl-phenyl bifunctional POSS; (f) periodic structure of pure PI system; (g) periodic structure of chemical bonding system and (h) periodic structure of physical blending system.

tion of PI-containing POSS; in the physical blending system, the mass fraction was altered by adjusting the amount of POSS while ensuring that the number of molecular chains in both PI composite systems was 12 to prevent end effects. The initial densities for both composite systems were set at 1.35 g/cm³. Based on this, models of PI/POSS composite insulation materials were established, as shown in Figs. 2(g) and 2(h),

where the POSS mass contents obtained through physical blending are labeled WL-PI-POSS-5%, WL-PI-POSS-10%, WL-PI-POSS-15%, and WL-PI-POSS-20%; correspondingly, the chemical bonding systems are labeled HX-PI-POSS-5%, HX-PI-POSS-10%, HX-PI-POSS-15%, and HX-PI-POSS-20%. The periodic structure of pure PI is shown in Fig. 2(f). During the construction of the periodic structures, a cubic simulation box

with dimensions of 40 nm × 40 nm × 40 nm (volume = 6.4 × 10⁴ nm³) was set for all systems to ensure reliable molecular dynamics (MD) simulations by minimizing periodic boundary effects while balancing computational efficiency. Following the construction, energy optimization and equilibration were performed under NVT and NPT ensembles (1 MPa), after which the box dimensions exhibited slight variations (less than 2%) depending on the specific system (e.g., pure PI or PI/POSS with different POSS contents), while maintaining the initial density across all systems. This box size was chosen to be more than an order of magnitude larger than the characteristic dimensions of the PI chains (typically 2–5 nm for a degree of polymerization of 4) and POSS molecules (1–2 nm), as well as the typical cutoff radius for non-bonded interactions (around 1.2 nm), ensuring minimal boundary effects and allowing for an accurate representation of bulk properties such as density, glass transition temperature (T_g), dielectric constant, and thermal conductivity.

The constructed models may have had issues such as configurational distortion and inappropriate interatomic distances. Therefore, after model construction was completed, energy optimization and equilibrium assessment of the PI composite system under molecular dynamics simulation were performed. During the molecular dynamics simulation process, the following module parameters were selected: the COMPASS force field was used, the NPT ensemble was employed, the electrostatic calculation method was Ewald, the van der Waals forces were modeled based on the atoms, an applied pressure of 1 MPa was set, the temperature control method was Andersen, and the pressure control method was Berendsen. A time step of 1 fs was chosen to ensure numerical stability, accommodating the high-frequency vibrations of light atoms (e.g., hydrogen) in the PI and POSS structures, which is a standard practice in polymer MD simulations. The equilibration process consisted of two steps: an initial energy minimization using the steepest descent method to eliminate unfavorable contacts, followed by a 100 ps NPT equilibration at 1 MPa and 300 K. The 100 ps duration was suffi-

cient, as the system's density and total energy converged to within 1% after approximately 80 ps, confirming that equilibrium was achieved. Subsequent production runs were conducted for 500 ps to collect data for the analysis of dielectric, thermal, mechanical, and degradation properties. Ultimately, Fig. 3 illustrates the periodic structure diagrams of physical blending and chemical bonding systems at various mass fractions, with the temperature and energy of each periodic structure model having reached equilibrium conditions.

Calculation of the Key Performance Parameters

Method for calculating the dielectric constant

To evaluate the dielectric properties of the composite materials, molecular dynamics simulations were applied after the models were constructed for each system to simulate the relaxation process under an external electric field. In the simulation, the total dipole moment of the system was obtained by calculating the dipole moment of each atomic block and averaging it over time. Based on the statistical data of the dipole moment, the polarization intensity could be calculated as the ratio of the average dipole moment to the volume. By relating the polarization intensity to the external electric field, the dielectric constant of the composite system could be calculated. The calculation principle is given by the following formula:

$$\epsilon_0 = 1 + \frac{1}{3V\kappa_B T_e} ([M^2] - [M]^2) \quad (4)$$

where M is the dipole moment obtained from each calculation; $[M^2]$ is the mean square of the one-step axial displacement average during the simulation process; $[M]^2$ is the square of the mean of the one-step axial displacement; V is the volume of the simulation system; T_e is the temperature of the simulation system; ϵ_0 is the vacuum permittivity and is approximately equal to 8.854 × 10⁻¹² F/m; and κ_B is the Boltzmann constant and is approximately equal to 1.381 × 10⁻²³ J/K.

Method for calculating the thermal conductivity

The thermal conductivity is calculated via the Muller–Plathe

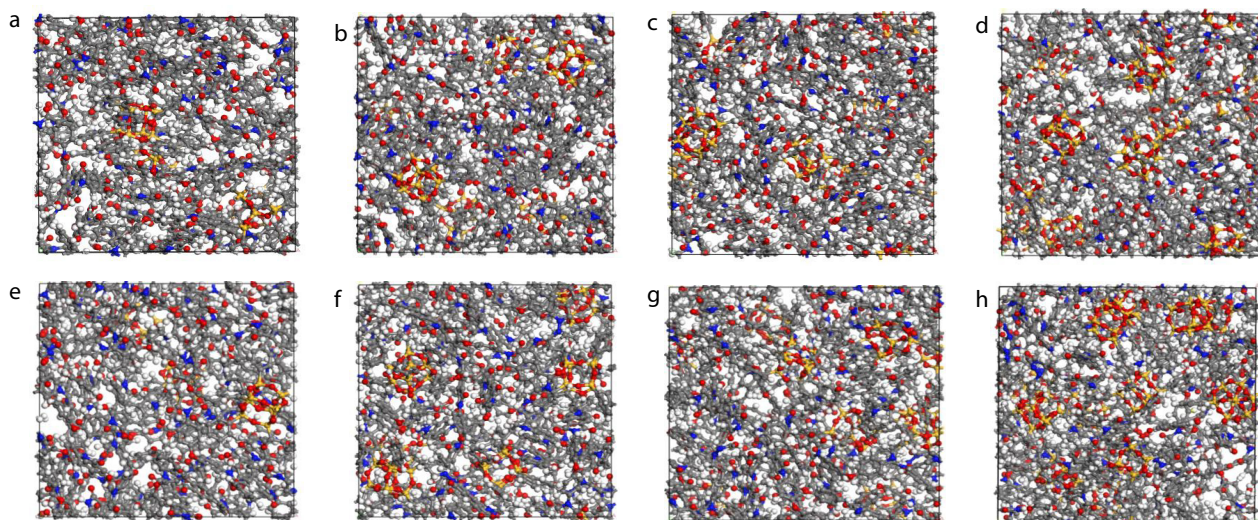


Fig. 3 Periodic structure diagrams of pure PI and PI/POSS composite systems with POSS mass fractions of 5 wt%–20 wt% via molecular dynamics simulations: (a–d) periodic structures of physical blending PI/POSS systems: (a) 5 wt% POSS, (b) 10 wt% POSS, (c) 15 wt% POSS, (d) 20 wt% POSS; (e–h) periodic structures of chemical bonding PI/POSS systems: (e) 5 wt% POSS, (f) 10 wt% POSS, (g) 15 wt% POSS, and (h) 20 wt% POSS.

method, which is a technique used in molecular dynamics simulations. This method introduces heat sources and cold sources to create a significant temperature difference and quantifies the heat flow using the temperature gradient to calculate the thermal conductivity. Specifically, the system is divided into 20 regions along the z-axis, with heat sources (350 K) applied at one end and cold sources (250 K) at the other. Langevin dynamics is used to control the temperature to maintain the temperatures of the heat and cold sources, driving heat flow. During the simulation, the vibrational information of the atoms in the material (temperature, position, and velocity) is recorded, and the kinetic energy of each atom is calculated to estimate the heat flow based on the changes in kinetic energy. The temperature gradient is determined by performing block temperature calculations between the heat and cold sources. Finally, by conducting block calculations and time averaging, the heat flux density and temperature gradient of the system are obtained, from which the thermal conductivity can be derived. The thermal conductivity (k) can be expressed using Fourier's law, as follows:

$$k = -\frac{q}{\nabla T} \quad (5)$$

where q is the heat flux density, and ∇T is the temperature gradient.

Interfacial adhesion energy assessment method

First, the interfacial adhesion energy model is constructed as shown in Fig. 4; here, the appropriate POSS monomers and pure PI were added on either side of the interface and labeled as modules A and B for the simulation of the interfacial structure under examination. The geometric shape and interactions of the interface model were designed to be consistent with those of the actual system. After the model was constructed, molecular dynamics simulations were conducted under the NVT ensemble. Based on the molecular dynamics simulations, the energies of the stable structures of A and B before bonding, denoted as E_A and E_B , were obtained, as well as the energy of the stable conformation of the system AB after bonding, denoted as E_{A-B} . The interfacial adhesion energy could then be calculated using the following formula:

$$E_{\text{int}} = E_{A-B} - E_A - E_B \quad (6)$$

where E_{A-B} represents the total energy of the interface between POSS and PI; E_A and E_B refer to the energies of their respective stable structures; and E_{int} is the interfacial adhesion energy, which is the energy formed at the interface of the model.

Calculation methods for mechanical properties: Poisson's ratio and Young's modulus

In molecular dynamics simulations, the stiffness coefficient C_{ij} can be calculated by precisely controlling the strain and recording the corresponding stress. The stiffness matrix is constructed based on these stiffness coefficients, allowing Poisson's ratio and Young's modulus of the PI composite system to be determined. For isotropic materials, their stress-strain behavior can be described by only two independent coefficients: (1) the Lamé parameter λ and (2) the Lamé parameter μ . In this case, the stiffness matrix can be expressed as follows:

$$\begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \quad (7)$$

The PI composite system obtained from the molecular dynamics simulations closely resembles an isotropic material, and the numerical characteristics of the stiffness matrix highly overlaps with those of the isotropic stiffness matrix. Therefore, the Lamé parameters can be determined based on the relationships between the Lamé parameters and the matrix coefficients. Young's modulus E and Poisson's ratio ν of the composite system can subsequently be calculated using the Lamé parameters. The formulas used for these calculations are as follows:

$$\lambda = \frac{1}{3} (C_{11} + C_{22} + C_{33}) - \frac{2}{3} (C_{44} + C_{55} + C_{66}) \quad (8)$$

$$\mu = \frac{1}{3} (C_{44} + C_{55} + C_{66}) \quad (9)$$

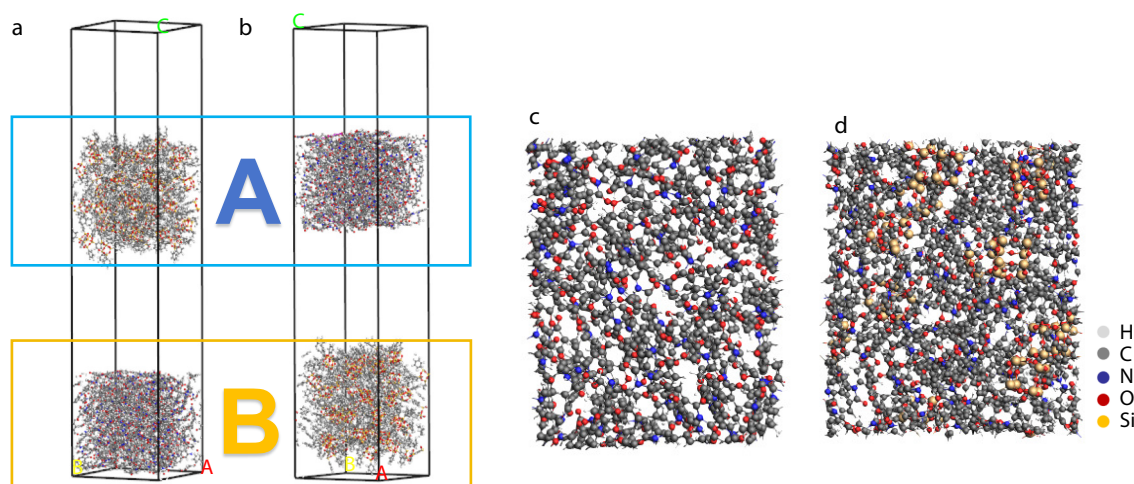


Fig. 4 Interface binding energy and cleavage model diagram: (a) physical blending interface binding energy model; (b) chemical bonding interface binding energy model; (c) pure PI model and (d) physical blending PI/POSS composite system model.

$$E = \mu \left(\frac{3\lambda + 2\mu}{\lambda + \mu} \right) \quad (10)$$

$$\nu = \frac{\lambda}{2(\lambda + \mu)} \quad (11)$$

where C_{ij} is the elastic constant of the material; λ represents the first Lamé parameter and describes the relationship between the volumetric change in the material and the stress; μ denotes the shear modulus of the material (also known as the second Lamé parameter) and reflecting the material's ability to respond to shear strain; E is Young's modulus of the material and characterizes its strain capacity under axial stress; and ν is Poisson's ratio, which is the ratio of the lateral strain to the axial strain in the material.

Method for determining the glass transition temperature

The glass transition temperature (T_g) refers to the temperature at which a polymer transitions from a hard and brittle glassy state to a soft rubbery state. In the molecular dynamics simulations, the density of the PI composite system is calculated at different temperatures to obtain the specific volume, allowing for the construction of a curve that shows the variation in molar volume with temperature. The glass transition temperature corresponds to the inflection point of this curve; this temperature indicates a significant increase in the mobility of the polymer chain segments and a change in the material properties. Using this method, the glass transition temperature of a material can be accurately determined.

Specifically, molecular dynamics simulations are conducted at 300 K under the NVT ensemble, with a simulation duration of 500 ps to relax the polymer chains and prepare for subsequent stepwise cooling simulations. The equilibrated conformations from the NVT molecular dynamics simulation are then used as the starting point for the subsequent NPT molecular dynamics simulations. The temperature starts at 300 K and is increased by 100 K at each step until it reaches 900 K, resulting in 8 stages. The above steps are repeated and then gradually cooled from 900 K to 300 K; during this process, molecular dynamics simulations are performed, and the data are extracted from the cooling phases for the subsequent calculations of specific volume to ultimately determine the glass transition temperature for each system.

Research Methods for the Fracture Mechanism under High Temperature and Strong Electric Field Conditions

To investigate the fracture mechanism of the PI/POSS composites under high temperatures and strong electric fields, reactive force field (ReaxFF) to simulate the processes of bond formation and breaking during the chemical reactions; thus, a more accurate description of the structure and properties of complex molecular systems is provided.^[27] The ReaxFF force field is a specialized reactive force field that dynamically adjusts the interactions between the atoms to handle the processes of bond breakage and the formation of new bonds; hence, it is widely applicable in computational simulations of material science and chemical reactions. Its core concept is to decompose the total energy of the system into a sum of various bond-level interaction energies, including bond energies, lone pair electron energies, and van der Waals interaction energies.^[28]

Based on the research foundations in the relevant literature, molecular dynamics simulations were performed under high-temperature and strong electric field conditions of 2000

K and 0.04 V/Å, respectively.^[29–33] At high temperatures, the molecular kinetic energy increases, enhancing the thermal motion and significantly increasing the rate of chemical reactions. Thus, reactions occur more rapidly, enabling the observation of the phenomena such as bond breakage, recombination, and new bond formation within a shorter time frame. However, high temperatures do not affect the ultimate outcome of the reactions; the products still depend on the nature of the reactants and the reaction mechanisms. Therefore, selecting a high temperature of 2000 K not only accelerates the reaction rate but also provides richer information for understanding the degradation mechanisms of PI. The electric field strength is set at 0.04 V/Å and is calculated based on the initial discharge voltage measured for the Kapton PI films in local discharge experiments (approximately 1.3 kV).^[34]

First, a cubic model of PI and a cubic model of the PI/POSS composite system formed through physical blending were constructed, as shown in Figs. 4(c) and 4(d). The constructed models have high energy and are in an unstable state; thus, relaxation reactions on the models need to be performed to minimize the system's energy. Then, under the conditions of 2000 K and 0.04 V/Å, molecular dynamics simulations of 500 ps were conducted on the PI cubic model and the PI/POSS composite system cubic model using the isothermal-isochoric NVT system. The 500 ps simulation time is sufficient to capture the formation of primary degradation products and is also sufficiently long to describe the dynamic pathways and product distributions of the composite system under high-temperature and strong electric field conditions to examine the microscopic mechanisms of electrothermal aging of the composite materials.

RESULTS ANALYSIS

Key Performance Parameters of the PI Composite Systems

Dielectric constant results from the PI composite systems

To ensure the accuracy of the computational results, the dielectric constant of each system model were calculated using five simulations, and the average values were then calculated. The dielectric constant of pure PI was 3.6517 ± 0.072 , and the dielectric constants for the other systems are shown in the following line in Fig. 5(a).

With increasing mass fraction of POSS, the dielectric constant of the composites tended to decrease; this phenomenon was validated via both physical blending and chemical bonding methods and indicated that the introduction of POSS significantly improved the dielectric performance. At the same POSS mass fraction, the chemical bonding system generally had a lower dielectric constant, demonstrating its advantages in enhancing electrical performance. For example, when the POSS content was 5%, the dielectric constant of the chemical bonding system decreased from 3.652 ± 0.072 to 2.927 ± 0.081 ; however, a higher POSS content could lead to a slower rate of decrease. When the POSS content was 20%, the dielectric constants of both systems decreased to approximately 2.6.

The variation in the dielectric constant was closely related to the interactions between POSS and the PI molecular chains. The inorganic core of POSS increased the porosity and

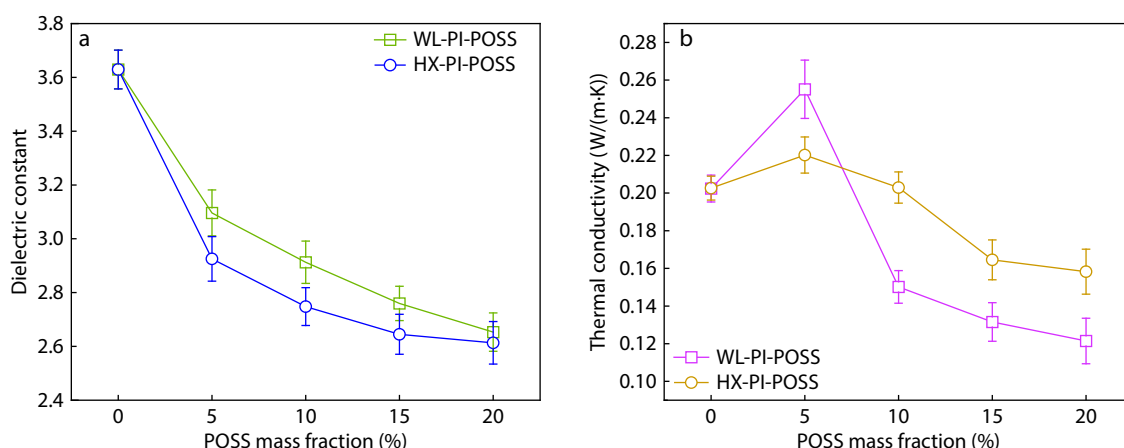


Fig. 5 (a) Dielectric constants of PI composite systems and (b) thermal conductivities of PI composite systems.

flexibility of the polymer chains; this reduced the polarization effects and decreased the interactions between the PI segments, thereby lowering the overall polarization intensity. Additionally, the uniform nanoscale pores of POSS introduced air, further reducing the dielectric constant.

In chemical bonding, POSS was covalently bonded to the PI chains, forming a stable molecular network that reduced the incoherence of chain movement and prevented the agglomeration; this network could perform better in lowering the dielectric constant than physical blending. In physical blending, POSS particles could agglomerate, reducing contact with the PI chains and affecting the dielectric performance. In contrast, in chemical bonding, as the POSS content increased, the chemical network could restrict the movement of the PI segments. Therefore, the rate of decrease in the dielectric constant for both methods slowed at high POSS ratios.

Results from the thermal conductivity for the PI composite systems

The thermal conductivity data of the PI composite system calculated using molecular dynamics simulation are shown in Fig. 5(b). With increasing POSS content in PI, the thermal conductivity of the composite materials initially increases and then decreases. In the case of physical blending, when PI is doped with 5% POSS, the thermal conductivity increases from 0.203 ± 0.007 W/(m·K) to 0.258 ± 0.015 W/(m·K). However, as the proportion of POSS increases to 10%, 15%, and 20%, the thermal conductivity decreases to 0.153 ± 0.008 , 0.132 ± 0.010 and 0.123 ± 0.012 W/(m·K), respectively. The trend of the change in thermal conductivity under the chemical bonding method is similar, but the variation is less pronounced.

At low POSS contents, the increase in thermal conductivity occurs because POSS improves the microstructure of PI, enhances the connectivity of the thermal conduction pathways, increases interfacial interactions, and facilitates heat transfer. The relatively low ratio of POSS also maintains the flexibility of the polymer chains, further promoting heat flow. However, when the POSS content is too high, the decrease in thermal conductivity is caused by filler agglomeration, restricted movement of the PI segments, and increased porosity; all of these factors impede heat conduction. In chemical bonding systems, although agglomeration may occur, covalent bonds enhance the fixed connection between POSS and PI, improving the thermal stability and reducing agglomeration phe-

nomena. Therefore, while the thermal conductivity of both systems may decrease at high filler ratios, the chemical bonding system tends to be more stable in maintaining the overall thermal conductivity performance.

Overall, appropriate doping of POSS can significantly enhance the thermal conductivity of PI, and key factors are good dispersion and strong interfacial interactions. However, issues such as agglomeration and restricted segment movement at high doping ratios can lead to a decrease in thermal conductivity; therefore, these results can provide theoretical guidance for the optimized design of PI composites.

Results from the interfacial adhesion energy for the PI composite systems

The data shown in Table 1 were obtained from the molecular dynamics simulations. Each column in the table represents relevant energy terms, where E_{A-B} signifies the total energy of the interface between POSS and PI, while E_A and E_B are the energies of their respective stable structures. The final column, E_{int} , is the interfacial adhesion energy calculated using the formula and represents the energy formed at the interface of the model. The data in the table indicate that the average interfacial adhesion energy of the PI physical blending system is approximately -94.30 kcal/mol, whereas the interfacial adhesion energy of the PI chemical bonding system is approximately -83.610 kcal/mol.

As shown by the data in Table 1, the interfacial adhesion energy fluctuates under different conformations but remains relatively stable overall; these results indicate that both the physical blending and chemical bonding systems form relatively stable adhesion at the interface; this is beneficial to the overall performance of the composites. The negative value of the interfacial adhesion energy indicates that energy is released during the formation process at the interface, and a certain degree of attractive force is present and enhances the stability of the interface; additionally, the physical blending system has a slight advantage. A higher interfacial adhesion energy indicates stronger interfacial attraction, which helps to resist electrothermal aging effects under high-temperature and strong electric field conditions, thus prolonging the service life of the material.

Results from Poisson's ratio and Young's modulus for the PI composite systems

In the molecular dynamics simulations, the corresponding stiff-

Table 1 Interfacial adhesion energy data of the PI system.

Conformation number	Physical blending system				Chemical bonding system			
	E_{A-B} (kcal/mol)	E_A (kcal/mol)	E_B (kcal/mol)	E_{int} (kcal/mol)	E_{A-B} (kcal/mol)	E_A (kcal/mol)	E_B (kcal/mol)	E_{int} (kcal/mol)
1	-33594.310	-5304.840	-28195.310	-94.161	-33573.010	-5298.531	-28190.860	-83.615
2	-27225.220	-2434.851	-24696.170	-94.196	-26887.680	-2247.230	-24556.830	-83.628
3	-26594.580	-2017.408	-24483.000	-94.168	-26712.650	-2281.288	-24347.760	-83.609
4	-27922.400	-2711.270	-25116.960	-94.170	-27769.280	-2839.068	-24846.620	-83.594
5	-26829.880	-2223.776	-24511.220	-94.880	-26772.800	-2372.362	-24316.830	-83.611
6	-26631.150	-2164.522	-24372.410	-94.212	-26860.100	-2454.930	-24321.570	-83.601

ness coefficients C_{ij} can be obtained by precisely controlling the strain and recording the corresponding stress. The stiffness matrix is then constructed from the stiffness coefficients, enabling Poisson's ratio and Young's modulus of the PI composite system to be calculated. The stiffness matrix of the pure PI system is provided in Table 2.

As shown by the data in Table 2, the stiffness matrix closely resembles the numerical characteristics of an isotropic stiffness matrix; these results indicate that the PI composite system obtained from molecular dynamics simulations approximates isotropic materials. Thus, using the formulas, the Lamé parameters for the pure PI model were determined to be $\lambda = 4.828$ GPa, $\mu = 1.193$ GPa, $E = 3.342$ GPa, and $\nu = 0.401$. Similarly, using the aforementioned methods, Young's modulus and Poisson's ratio in various directions are plotted in Figs. 6(a) and 6(b).

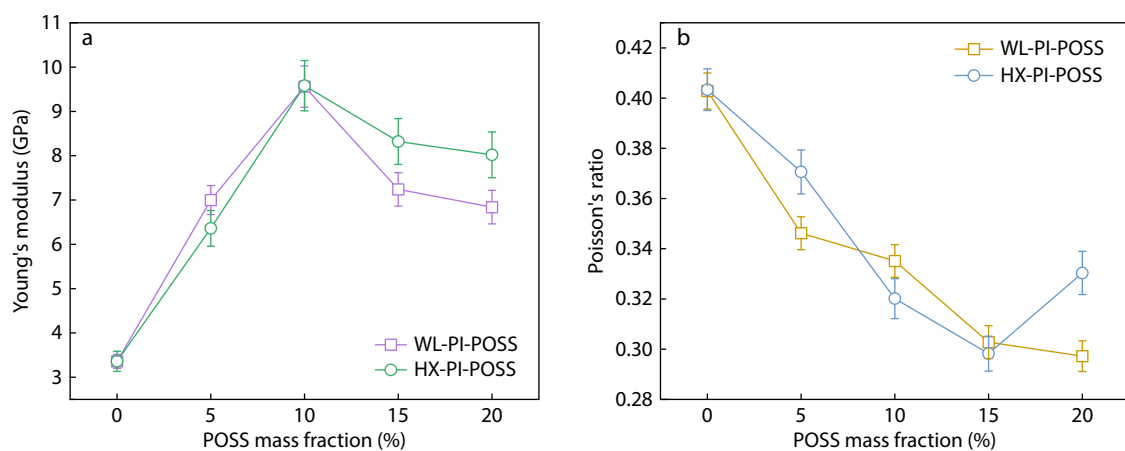
As shown in Fig. 6, Young's modulus in the physical blending and chemical bonding systems initially increases and then decreases but remains higher than that of pure PI. Notably, at higher mass fractions of POSS, Young's modulus of the chemical bonding system is significantly greater than that of the

physical blending system. When the POSS doping content is 5% and 10%, Young's moduli of both systems increase to approximately 6.5 and 9.5 GPa, respectively. However, as the mass fractions increase to 15% and 20%, Young's moduli decrease for both systems, and a more pronounced decline is observed with the physical blending method. The dispersion of POSS, the interfacial strength between the filler and the polymer matrix, and the motion of the polymer chain segments all affect the mechanical properties. An appropriate amount of POSS enhances the interfacial adhesion, improving the overall rigidity. However, higher filler concentrations may lead to agglomeration and interfacial inhomogeneity, thus restricting the free movement of the polymer chain segments and resulting in a decrease in Young's modulus.

As the mass fraction of POSS increases, Poisson's ratio tends to decrease. In the chemical bonding system, when the POSS doping content reaches 20%, Poisson's ratio slightly rebounds, which may be related to the increased interfacial strength and reduced segment mobility; this leads to a more stable structure of the polymer chains. In contrast, Poisson's ratio of the physical blending system decreases from

Table 2 Elastic stiffness matrix of the pure PI model.

C_{ij}	$j=1$ (xx)	$j=2$ (yy)	$j=3$ (zz)	$j=4$ (yz)	$j=5$ (xz)	$j=6$ (xy)
$i=1$ (xx)	8.3569	5.4936	3.7999	0.3697	-0.3306	0.1819
$i=2$ (yy)	5.4936	6.5261	5.3422	0.4285	-0.9547	-0.0101
$i=3$ (zz)	3.7999	5.3422	6.7629	1.1418	-0.1164	0.1657
$i=4$ (yz)	0.3697	0.4285	1.1418	1.0444	-0.4152	-0.2149
$i=5$ (xz)	-0.3306	-0.9547	-0.1164	-0.4152	1.1992	0.4855
$i=6$ (xy)	0.1819	-0.0101	0.1657	-0.2149	0.4855	1.3371

**Fig. 6** Line graphs of Young's modulus and Poisson's ratio for the PI composite system: (a) Young's modulus and (b) Poisson's ratio.

0.401±0.007 to 0.358±0.006, reflecting a decline in its structural load-bearing capacity. The decrease in Poisson's ratio mainly occurs because POSS doping enhances the interactions between the filler and the PI matrix; this increases the rigidity of the material and reduces lateral deformation. In the chemical bonding system, a higher POSS content strengthens the interfacial adhesion and helps the material to more effectively resist the tensile stress. However, in a physically blended system, the agglomeration of POSS can reduce the effective interactions between the polymer chain segments, thereby affecting the material's load-bearing capacity. In summary, the amount and dispersion of POSS significantly influence the changes in Poisson's ratio, reflecting the importance of the material's microstructural stability and performance optimization.

Results from the glass transition temperature for the PI composite systems

The glass transition temperature (T_g) of the PI composite systems was determined by analyzing the specific volume ($v=1/\rho$, in cm^3/g) as a function of temperature, as described in the section of 'Method for determining the glass transition temperature'. The plot of the specific volume versus temperature ob-

tained through molecular dynamics simulations reveals the simulated glass transition temperatures for each PI composite system, as shown in Fig. 7. Fig. 7(a) illustrates that T_g increases from 534 K for pristine PI to 701 K at 20 wt% POSS in the physical blending system (a rise of 167 K) and from 534 K to 739 K at 20 wt% POSS in the chemical bonding system (a rise of 205 K). To validate the T_g determination, Fig. 7(b) provides the specific volume versus temperature curves for the physical blending systems, including pure PI, WL-PI-POSS-5%, WL-PI-POSS-10%, WL-PI-POSS-15%, and WL-PI-POSS-20%, while Fig. 7(c) shows the specific volume versus temperature curves for the chemical bonding systems, including pure PI, HX-PI-POSS-5%, HX-PI-POSS-10%, HX-PI-POSS-15%, and HX-PI-POSS-20%. The inflection points on these curves, corresponding to the transition from glassy to rubbery states, confirm the T_g values reported in Fig. 7(a). In the PI composite systems, different methods of POSS doping (physical blending and chemical bonding) have a significant effect on the glass transition temperature (T_g). The observed increase in T_g with POSS doping, particularly pronounced in the chemical bonding system due to strong covalent crosslinking, aligns with enhanced intermolecular interactions and reduced chain mobility.

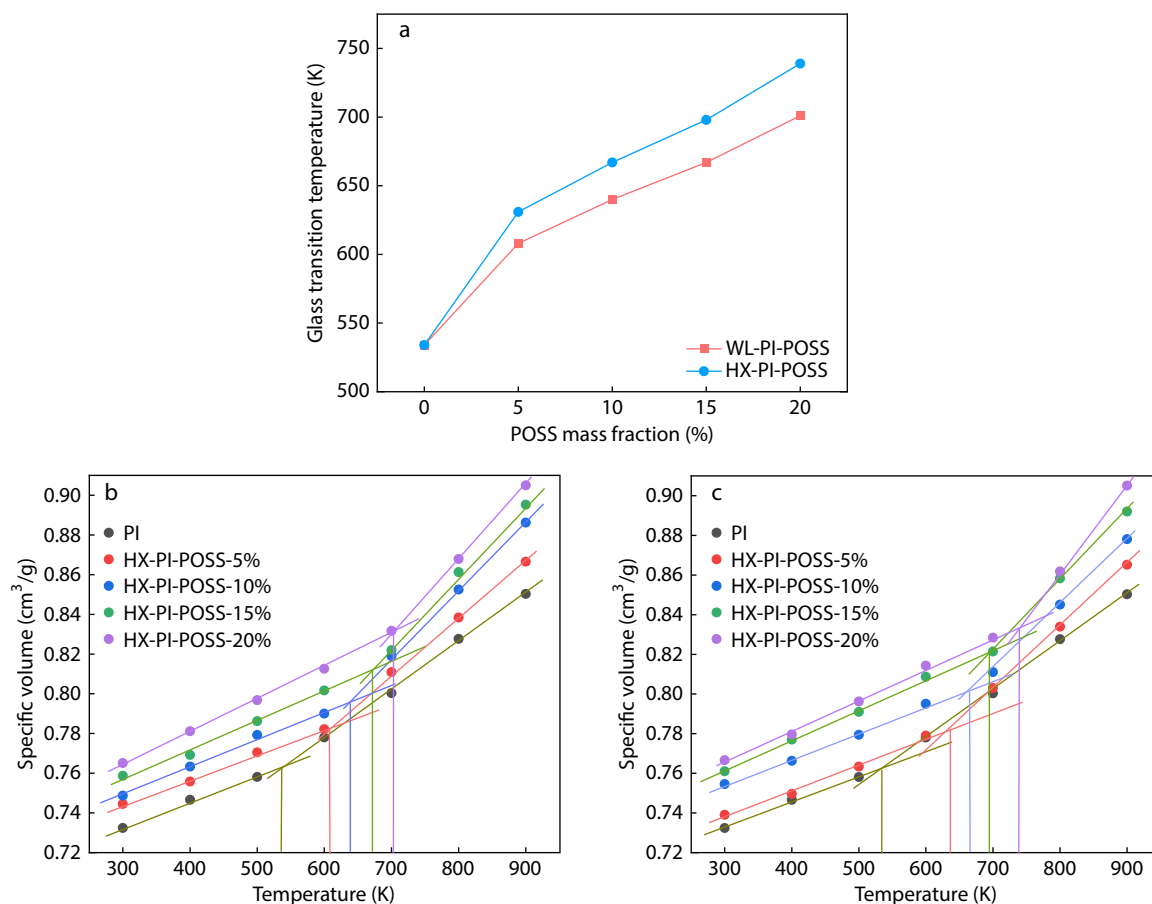


Fig. 7 Glass transition temperature and specific volume-temperature curves of PI-POSS composite systems via molecular dynamics simulations. (a) Simulated glass transition temperature (T_g) values for PI-POSS composite systems with varying POSS contents in physical blending (WL-PI-POSS) and chemical bonding (HX-PI-POSS) methods; (b) Specific volume versus temperature curves for physical blending systems, including pure PI, WL-PI-POSS-5%, WL-PI-POSS-10%, WL-PI-POSS-15%, and WL-PI-POSS-20%; (c) Specific volume versus temperature curves for chemical bonding systems, including pure PI, HX-PI-POSS-5%, HX-PI-POSS-10%, HX-PI-POSS-15%, and HX-PI-POSS-20%.

In the PI composite systems, different methods of POSS doping (physical blending and chemical bonding) have a significant effect on the glass transition temperature (T_g). In the physical blending system, as the POSS content increases, the T_g linearly increases from approximately 608 K at 5% to approximately 701 K at 20%, although the overall increase is relatively limited. In contrast, the increase in the glass transition temperature in the chemical bonding system is more pronounced, and T_g starts at 630 K at 5% POSS and reaches 739 K at 20% POSS, demonstrating a more significant increase.

This difference stems from variations in molecular interactions and material structures. In the chemical bonding mode, strong chemical cross-linking occurs between POSS and PI, significantly enhancing intermolecular interactions. This cross-linking restricts the movement of polymer chains through covalent bonds; this increases the material's rigidity and thermal stability and ultimately leads to a higher glass transition temperature. Specifically, in the chemical bonding system, polyhedral oligomeric silsesquioxane (POSS) is covalently bonded to polyimide (PI) chains via aminopropyl groups, forming a robust crosslinked network. This covalent integration restricts chain segment mobility through two primary mechanisms. First, the covalent bonds anchor PI chains to the rigid, cage-like POSS structures, significantly limiting the conformational dynamics of the polymer backbone. This anchoring effect hinders the independent rotation and sliding of chain segments, thereby increasing the energy required for the glass-to-rubber transition. Second, the incorporation of rigid POSS units introduces steric hindrance and enhances the local rigidity of the PI matrix. This elevates the energy barrier for cooperative segmental motion—a key process in the glass transition—necessitating higher thermal energy for chain relaxation. Consequently, T_g increases substantially from 534 K for pristine PI to 739 K at 20 wt% POSS, a rise of 205 K, underscoring the effectiveness of covalent crosslinking in constraining chain dynamics.

In the physical blending system, POSS interacts with PI through secondary bonds; here, the intermolecular connections are improved, but the interaction between POSS and PI is relatively weak and does not effectively enhance the overall stability of the polymer. Although the T_g increases with increasing POSS content, the effects are limited by the phase separation and incomplete bonding. Additionally, the presence of secondary bonds does not effectively inhibit the movement of molecular chains, further hindering the increase in the T_g . In contrast, the physical blending system relies on weaker van der Waals interactions between POSS and PI, resulting in a less pronounced restriction of chain mobility. First, without covalent linkages, POSS acts as a dispersed filler within the PI matrix, providing only transient resistance to chain motion through physical entanglements and increased local density. The absence of permanent anchoring allows PI chains to retain greater mobility compared to the chemical bonding system. Second, POSS molecules in the physical blending system are not fixed to the PI chains and can migrate within the matrix. At higher POSS contents (15 wt%–20 wt%), aggregation may occur, reducing the uniformity of POSS-PI interactions and further diminishing the constraint on chain dynamics. As a result, T_g in the physical blending sys-

tem increases more modestly, from 608 K at 5 wt% POSS to 701 K at 20 wt% POSS—a total rise of 167 K, which is notably lower than the 205 K increase observed in the chemical bonding system, highlighting the limited efficacy of physical interactions in restricting chain motion.

At 20 wt% POSS, the chemical bonding system achieves a T_g of 739 K, exceeding the 701 K of the physical blending system by 38 K. This 38 K difference underscores the superior ability of covalent crosslinking to enhance thermal stability. The enhanced restriction in the chemical bonding system arises from the permanent anchoring of PI chains to POSS, in contrast to the transient and less effective interactions in the physical blending system, where POSS mobility and potential aggregation reduce its impact on chain dynamics. These findings highlight the potential of covalent crosslinking strategies for designing PI composites tailored for high-temperature applications, such as electrical insulation materials, where a higher T_g ensures enhanced mechanical integrity and thermal resistance at elevated temperatures, thus expanding the practical utility of these materials.

In summary, the chemical bonding method markedly enhances the glass transition temperature of the PI composites through robust chemical cross-linking and enhanced interactions, whereas the effects of physical blending are more limited due to structural inhomogeneity and weak interactions. This comparative result provides valuable theoretical guidance for optimizing the performance of PI composites.

Research Results on the Fracture Mechanisms of the PI/POSS Composites under High Temperature and Strong Electric Field Conditions

Owing to the simplicity of the physical blending process, low equipment requirements, and strong processing compatibility, this method is more commonly used in industrial applications. Furthermore, based on their calculated performance parameters, the PI/POSS composites formed by physical blending significantly reduce the dielectric constant when the mass fraction of POSS is approximately 5%. Compared with the chemical bonding method, physical blending also enhances the thermal conductivity of the composites to a greater extent and results in superior performance in the other parameters. Therefore, the degradation behavior of pure PI systems and PI/POSS composite systems formed by physical blending under high-temperature and strong electric field conditions are investigated. By thoroughly examining the degradation dynamic pathways and product distributions of these two systems, the aim is to reveal the microscopic mechanisms of the composites during the electrothermal aging process.

Analysis of the fracture simulation results of the PI/POSS composites under high temperature

From the structures of the PI monomer and the POSS monomer, nine types of chemical bonds are present in their molecular structure: C—C, C = O, C—O, C—N, C—H, C—Si, O—Si, C = C, and the large π bonds in the benzene ring. Among these, the C = O bond has the highest bond energy and requires more energy to break, whereas the C—N bond has the lowest bond energy at 305 kJ/mol and requires less energy to break. Fig. 8 shows the variation in the main degradation products of the pure PI system and the PI/POSS composite system formed by physical blending over time at 2000 K.

Fig. 8 reveals that the primary degradation products of the pure PI system and the PI/POSS composite system, formed by physical blending at 2000 K, are CO and H₂O, with their fractions rising progressively over the 500 ps simulation. In the pure PI system, the average molecular number percentages of CO and H₂O over the 500 ps reaction time are 31.66% and 1.44%, respectively, relative to the total number of degradation product molecules, whereas in the PI/POSS composite system, these fractions are 25.63% for CO (representing a 19% relative decrease) and 3.21% for H₂O (representing a 123% relative increase). This demonstrates that POSS effectively suppresses CO production while enhancing H₂O formation. The decreased CO production results from POSS improving the structural stability of the composite, which inhibits the cleavage of bonds (e.g., C—C and C—O) responsible for CO formation, while promoting pathways favoring H₂O production. However, CO levels in both systems continue to rise due to the ongoing decomposition of unreacted intermediates, such as large molecular fragments (e.g., C₄₃H₁₉N₄O₁₀) from PI chain cleavage, which undergo secondary reactions

involving C—N and C—O bond cleavage to yield additional CO. Despite this persistent CO increase, POSS sustains its suppression effect by maintaining structural stability and redirecting reaction pathways, as shown in Fig. 9, where POSS facilitates the formation of oxygen-containing intermediates, diverting a portion of the degradation pathway flux toward H₂O and other non-CO products, thereby consistently reducing CO emissions even as intermediates continue to decompose.

The degradation dynamic pathways of the pure PI system and the PI/POSS composite system formed by physical blending under high temperatures and strong electric fields are analyzed; the results reveal that both systems exhibit similar dynamic pathways for the generation of CO and H₂O under high-temperature conditions. Pathways (a) → (b) → (c) in Fig. 9 correspond to the pathway for producing CO at 2000 K. Under the high-temperature condition of 2000 K, the N—C bond between the carbon and nitrogen atoms in the PI molecular chain is the first to break; this result aligns with the observation that the N—C bond has the lowest bond energy

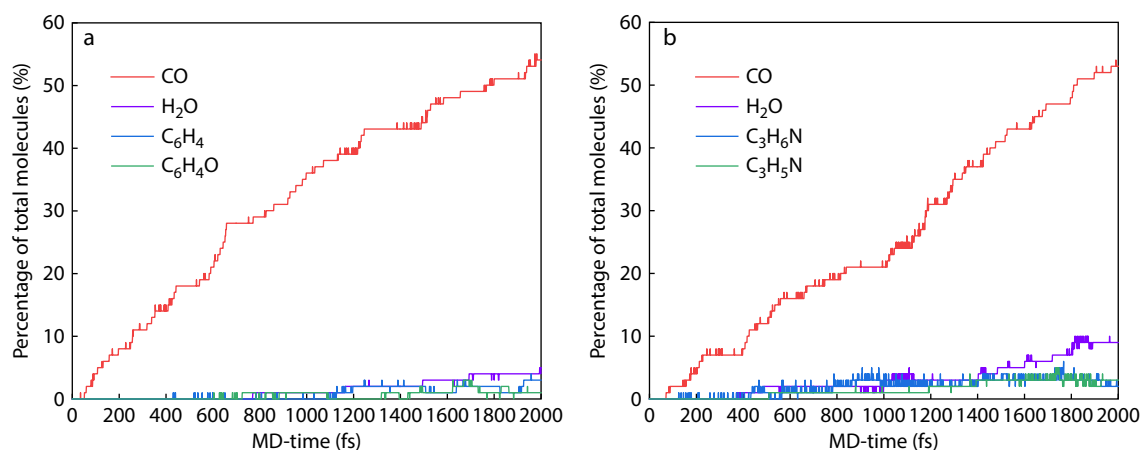


Fig. 8 Main degradation products of the composite system at 2000 K: (a) pure PI system and (b) physical blending system.

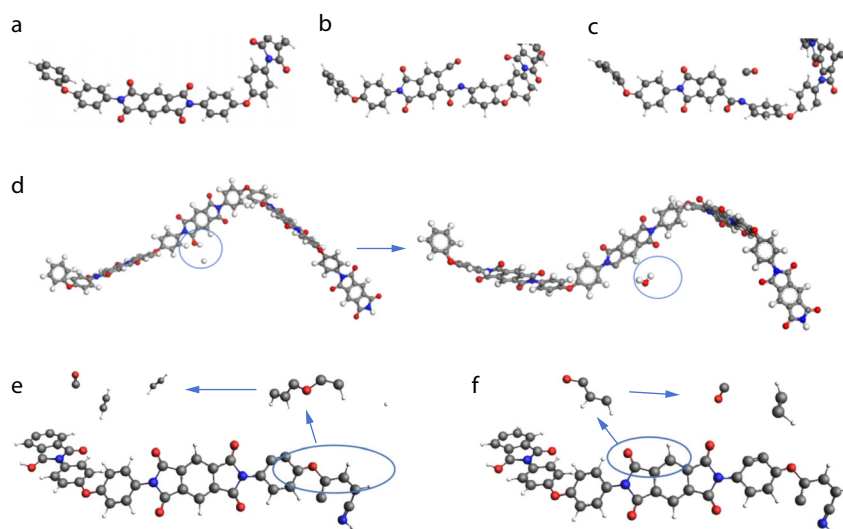


Fig. 9 Schematic diagram of the pathway: (a) complete PI model; (b) breakage of the N—C bond; (c) breakage of the C—C bond; (d) C—O=O double bond converging to the C—O single bond; OH combines with H to form a water molecule; (e) pathway 1 for the generation of CO and C₂H₂ and (f) pathway 2 for the generation of CO and C₂H₂.

in the PI molecular chain. After the N—C bond breaks, the C—C bond of the carbon atom connected to the oxygen atom also breaks, resulting in the formation of CO. This pathway is the primary source of CO at 2000 K.

Pathway (d) corresponds to the breaking of the C—O bond between the carbon and oxygen atoms in the PI molecular chain and the formation of water molecules. As shown in Fig. 9, the C = O double bond is converted into a C—O single bond because of the presence of incoming hydrogen atoms. At the same time, the hydrogen atom forms an O—H bond with the oxygen atom. The C—O bond subsequently breaks, resulting in the combination of OH with H to form water molecules.

According to the above data, the primary degradation products of both the pure PI system and the PI/POSS composite system formed by physical blending are CO and H₂O, and both have fundamentally similar degradation pathways. However, the amount of CO generated in the PI/POSS composite system formed by physical blending is significantly lower than that in the pure PI system, whereas the generation of H₂O is noticeably greater. This occurs because the incorporation of POSS improves the interfacial adhesion strength and stability of PI and inhibits the breaking of certain chemical bonds, particularly the C—N or C—C bonds, thus reducing CO production. Additionally, the doping of POSS leads to the formation of more oxygen-containing intermediates; these intermediates preferentially generate water through specific reaction steps. This phenomenon indicates that the introduction of POSS provides a noticeable environmental advantage in reducing harmful gas emissions *via* the physical blending method.

Analysis of the fracture results of the PI/POSS composites under strong electric field conditions

Fig. 10 shows the variation in the main degradation products of the pure PI system and the PI/POSS composite system formed by physical blending over time under strong electric field conditions.

As shown in Fig. 10, under strong electric field conditions, the main degradation products formed by physical blending are CO, HO, and C₂H₂ for the pure PI system and CO, H₂O, and C₂H₂ for the PI/POSS composite system. In the pure PI system, the average molecular number percentages of CO, HO, and C₂H₂ over the 500 ps reaction time are 15.45%, 4.47%, and 3.55%, respectively, relative to the total number of degradation product molecules. In the PI/POSS composite system formed by physical blending, the average molecular number percentages of CO, H₂O, and C₂H₂ over the 500 ps reaction time are 10.25%, 5.97%, and 2.60%, respectively, relative to the total number of degradation product molecules.

Under the influence of a strong electric field, the reaction pathways for the generation of CO and C₂H₂ in both systems also show similarities, as illustrated in Figs. 9(e) and 9(f). According to Fig. 9, the oxygen atom in the PI molecular chain can be in two different positions: in position one, the oxygen atom is located between two benzene rings, and in position two, the oxygen atom is connected to the carbon atom in the C—N bond. Under strong electric field conditions, the PI molecular chain breaks, producing many intermediates. Certain chemical bonds within the PI molecular chain (such as

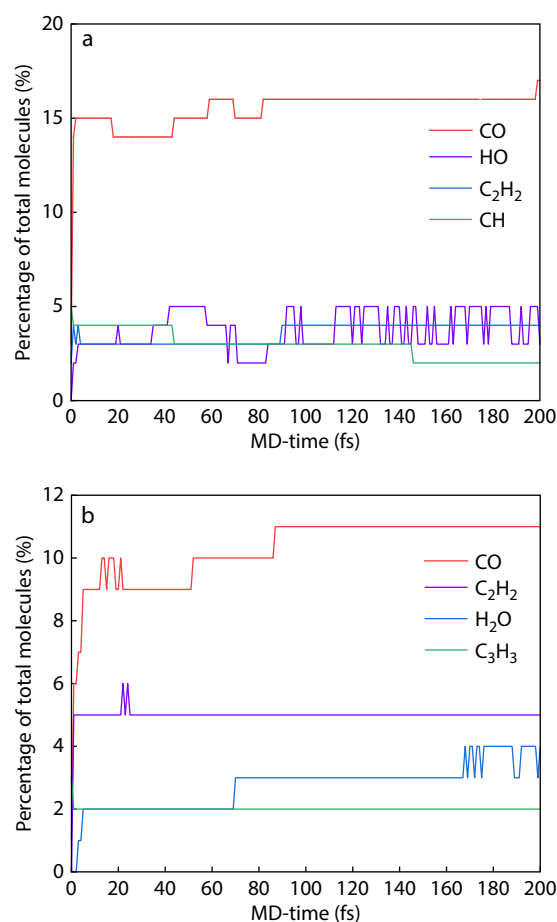


Fig. 10 Main degradation products of the composite system under strong electric field conditions: (a) pure PI system and (b) physical blending system.

C—N or C—C bonds) begin to break when subjected to a strong electric field, leading to disruption of the chain's integrity and the gradual release of small molecules or other products. The oxygen atoms in the two positions are particularly conducive to forming the intermediates shown in Fig. 9. For example, in Pathway 1, the cleavage of the C—O and C—C bonds results in the generation of CO and C₂H₂. In Pathway 2, the cleavage of the C—C bond also produces CO and C₂H₂. According to the product distribution graph, under the cleavage conditions of a strong electric field, the amount of CO generated in the PI system doped with POSS is notably lower, whereas the generation of H₂O significantly increases. Analysis of multiple reaction data clearly indicates that this trend is also attributed to the incorporation of POSS. POSS significantly enhances the interfacial adhesion strength and stability of PI, effectively inhibiting the cleavage of critical chemical bonds, reducing the production of CO and promoting the formation of water. These results further confirm the positive role of POSS in improving material properties and environmental characteristics.

In summary, the degradation behavior of the PI system doped with POSS under high-temperature and strong electric field conditions involves a more complex reaction mechanism than that of pure PI. Our results aid in the understand-

ing of the changes in the performance in practical applications and the reduction in the environmental impact. This phenomenon has significant environmental implications; reducing the generation of CO aids in lowering harmful gas emissions and improving air quality. Additionally, the increased production of water molecules indicates a cleaner reaction process, which helps reduce toxicity and pollutant generation and contributes to environmental protection and sustainable development.

CONCLUSIONS

In this study, molecular dynamics simulation methods are innovatively used to systematically investigate the properties of PI/POSS composites and their degradation mechanisms under high-temperature and strong electric field conditions, and their application and optimization potential in harsh environments such as high-frequency power transformers are highlighted. The significant advantages of POSS doping in enhancing the performance of PI is demonstrated. Specifically, when the mass fraction of POSS is approximately 5% to 10%, the composite materials show notable improvements in their dielectric performances while also enhancing their thermal conductivities and other properties to some extent. Doping with POSS significantly lowers the dielectric constant of PI, and the composite material's dielectric constant decreases to 2.6 at a POSS mass fraction of 20%. However, as the mass fraction increases, the rate of decrease in the dielectric constant slows due to agglomeration and other factors. The thermal conductivity of the composite system initially increases and then decreases with increasing POSS content, and the physical blending system shows more pronounced changes; the thermal conductivity reaches 0.258 W/(m·K) at 5% POSS doping.

In terms of mechanical properties, POSS doping effectively enhances Young's modulus; however, at higher mass fractions (15%–20%), Young's modulus decreases, and Poisson's ratio generally decreases. Conversely, Poisson's ratio for the chemical bonding system slightly increases at 20% doping. In the PI composite systems, the chemical bonding method significantly increases the glass transition temperature from 630 K at 5% to 740 K at 20%, primarily due to strong chemical cross-linking and enhanced intermolecular interactions. While the physical blending method also increases T_g , the overall increase is relatively limited and reaches a maximum of only 700 K because of weaker interactions and potential phase separation.

In addition, doping with POSS under high-temperature and strong electric field conditions improves the interfacial adhesion strength and stability of PI, suppresses the breakage of key chemical bonds, reduces the generation of harmful gases, and promotes the formation of water molecules. Due to these environmentally friendly characteristics, the PI/POSS composites can be applied more safely under high temperatures and strong electric field conditions and contributes to the trends of sustainable development and environmental protection.

In summary, a solid theoretical foundation and practical guidance for engineering applications of high-frequency power systems is provided, and these composites have

tremendous value in enhancing material performance, environmental advantages, design optimization, and extensive application potential. By combining innovative methods of physical blending and chemical bonding and considering the trade-offs among the various performance parameters, this research provides new concepts for future material design. This approach enables precise adjustments of the doping ratio and dispersion method of POSS based on the specific needs, thereby increasing the suitability of engineering materials. The research findings not only apply to power transformers but can also be extended to high-tech fields such as the aerospace, electronics, and automotive industries. In particular, in high-temperature and strong electric field environments, PI/POSS composites are expected to become the preferred choice for a new generation of insulating materials.

To further enhance the performance of polymers and broaden their applications, future research needs to focus on the following directions. First, the doping ratio and dispersion method of POSS need to be optimized to avoid agglomeration, and the impact of uniform filler distribution on the composite performance needs be explored. Second, investigations of more high-quality fillers and assessments of their potential in PI-based composites are needed. Third, more detailed studies on mass fractions, including lower doping ratios, need to be conducted to gain a deeper understanding of the effects of doping on the material properties. Finally, experimental validation and long-term performance investigations need to be promoted to confirm the reliability of the simulation results, and research findings for the sustainable development should be applied to provide environmentally friendly material solutions. In summary, future research will focus on these issues to address the shortcomings of the current study.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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