Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Molecular Dynamics and Experimental Investigation of TOTM-Plasticized EPDM Rubber for Sealing-Related Mechanical Performance

Wanjia Sheng
Yanfeng Xing
smsmsues@163.com

Shanghai University of Engineering Science - Songjiang Campus: Shanghai University of Engineering Science https://orcid.org/0009-0007-8249-6378
Fuyong Yang
Juyong Cao
Ying Wang
Xiaobing Zhang

Research Article

Keywords: EPDM rubber, trioctyl trimellitate, molecular dynamics simulation, stress relaxation, sealing-related mechanical performance

Posted Date: June 16th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-9866722/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Molecular Dynamics and Experimental Investigation of TOTM-Plasticized EPDM Rubber for Sealing-Related Mechanical Performance

Wanjia Sheng, Yanfeng Xing, Fuyong Yang, Juyong Cao, Ying Wang, and Xiaobing Zhang*

School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

Address correspondence to E-mail: smsmsues@163.com

ABSTRACT: Ethylene propylene diene monomer rubber (EPDM) is widely used in sealing-related applications where flexibility, compression recovery, and stress retention are critical for long-term compressive service. In this work, trioctyl trimellitate (TOTM) was introduced as a plasticizer to prepare TOTM/EPDM systems with different TOTM contents, and molecular dynamics simulations combined with experimental tests were used to investigate the resulting microstructural evolution, segmental motion, and mechanical response. The simulation results show that TOTM inserts into the interchain regions of EPDM and modifies the chain packing state. The fractional free volume (FFV) first decreases and then slightly recovers with increasing TOTM content, indicating the combined effects of interchain void filling and plasticization-induced relaxation. The mean square displacement (MSD), radial distribution function (RDF), coordination number, and radius of gyration (R_g) results further suggest that moderate TOTM contents promote

segmental mobility, effective local interactions, and relatively stable chain conformations. The simulated mechanical response and experimental results consistently demonstrate that TOTM reduces the stiffness, hardness, and stress at the same strain, while the elongation at break increases initially and then decreases. These results indicate that appropriate plasticization improves the flexibility and interfacial conformity potential of EPDM, whereas excessive TOTM may weaken interchain constraints and structural support. Overall, 15–20 wt% TOTM can be regarded as a candidate optimization range for TOTM/EPDM systems for sealing-related mechanical performance, with the formulation near 15 wt% showing a better balance among segmental mobility, flexibility, and compressive service stability.

KEYWORDS: EPDM rubber; trioctyl trimellitate; molecular dynamics simulation; stress relaxation; sealing-related mechanical performance

1 Introduction

Ethylene propylene diene monomer rubber (EPDM) is widely used in sealing-related applications because of its excellent heat resistance, weather resistance, chemical stability, and flexibility. In long-term compressive service, elastomeric sealing materials are required to maintain sufficient interfacial conformity, compression recovery, and stress retention. These requirements are particularly important in demanding sealing environments such as proton exchange membrane fuel cell (PEMFC) stacks, where the gasket must isolate hydrogen, air, and coolant channels while maintaining stable sealing contact pressure under compression, temperature fluctuations, and exposure to service media.

PEMFCs have attracted increasing attention in new energy vehicles, stationary energy storage, and hydrogen energy equipment owing to their high energy conversion efficiency, low operating

temperature, rapid dynamic response, and zero-emission characteristics. Recent reviews have indicated that the engineering development of PEMFCs has gradually shifted from improving individual core materials to the coordinated optimization of stack durability and reliability[1–3]. For transportation applications, the U.S. Department of Energy (DOE) has proposed that fuel cell systems should deliver 50% of their rated power within 30 s at −20 °C, which places higher requirements on the stability of peripheral sealing materials under low-temperature, compressive, and cyclic loading conditions[4]. A PEMFC stack is generally assembled by compressing multilayer components, including end plates, bipolar plates, gas diffusion layers, membrane electrode assemblies, and sealing gaskets[5–8]. Although sealing gaskets do not directly participate in electrochemical reactions, they play a crucial role in preventing cross-leakage of media and maintaining stable contact pressure[9]. With the continuous improvement of membrane electrodes and bipolar plates, the sealing system has gradually become one of the key factors affecting stack lifetime and reliability[10–13].

The performance of sealing gaskets depends strongly on the balance between interfacial adaptability and mechanical support. Interfacial leakage is not only related to clamping pressure, but is also affected by surface roughness and the viscoelastic behavior of gasket materials[11, 14–17]. A gasket material should be sufficiently compliant to adapt to microscopically rough interfaces, while also maintaining adequate stress retention to suppress stress relaxation and compression set during long-term compression. EPDM is an important candidate material for PEMFC sealing gaskets because its saturated main-chain structure provides good resistance to heat, weathering, and chemical corrosion. Tan et al. reported that EPDM exhibits good structural stability in simulated fuel cell environments involving humidity, heat, and chemical exposure[18]. Cui et al. demonstrated that EPDM exhibits pronounced stress relaxation under long-term

compression, which is significantly affected by temperature and strain level[19]. Furthermore, Shen et al. achieved coordinated optimization of hardness and compression properties of EPDM through a multilayer structural design[20], while Kusoglu et al. indicated that sealing geometry also plays an important role in gas tightness and durability[21]. These studies suggest that although EPDM possesses favorable basic properties, its sealing performance still requires further optimization through material modification.

One limitation of unmodified EPDM is that strong chain entanglement and interchain interactions restrict segmental mobility, resulting in insufficient flexibility under low-temperature or low-compression conditions. Plasticization is an effective strategy for regulating the flexibility and processability of rubber materials. Plasticizers can enter the interchain regions of polymers, weaken interchain interactions, increase local free space, and enhance segmental mobility, thereby reducing modulus and hardness while improving ductility[22]. However, the effect of plasticization is not always beneficial. Excessive plasticizer addition may weaken structural support, enhance chain slippage, and aggravate compression set and stress relaxation. Therefore, the plasticizer content must be optimized to balance flexibility improvement and mechanical support retention.

Trioctyl trimellitate (TOTM), as a high-molecular-weight ester plasticizer, has low volatility, low migration tendency, and excellent thermal stability, and is therefore considered more suitable for long-life sealing material systems[23, 24]. Lai et al. demonstrated in PVC systems that TOTM exhibits significantly low diffusion characteristics, which is beneficial for suppressing long-term migration[25]. Related studies have also indicated that high-molecular-weight plasticizers have advantages in maintaining mechanical properties and long-term stability. For the TOTM/EPDM system, TOTM can improve interfacial conformity by regulating interchain spacing and free

volume; however, excessive addition may lead to overly enhanced segmental mobility, thereby affecting compression performance. Existing studies on rubber plasticization further support this phenomenon. Tang et al. found through molecular dynamics simulations of DOP/NBR systems that DOP can significantly reduce hardness and improve ductility, while variations in DOP content lead to nonmonotonic changes in modulus and radius of gyration[26]. Similarly, Wang et al. investigated the free volume characteristics of ethylene propylene diene monomer rubber (EPDM) and their dependence on temperature and strain using molecular dynamics simulations, revealing the microscopic mechanism of its viscoelastic behavior[27]. These studies collectively indicate that plasticizer action involves an optimal content window rather than a simple linear relationship.

Molecular dynamics simulation provides an effective approach for understanding the microscopic origin of macroscopic property changes. Compared with macroscopic experiments, molecular simulations can reveal how plasticizers affect free volume, segmental motion, local interactions, and chain conformation at the atomic or molecular scale. He et al. developed a tannic-acid-based multi-mechanism biomass antioxidant through a combination of experiments and molecular simulations, significantly improving the thermo-oxidative aging resistance of nitrile butadiene rubber[28]. This demonstrates that combining molecular simulation with experimental validation is useful for establishing microstructure–property relationships in rubber materials.

Although plasticized rubber systems such as NBR and PVC have been widely studied, systematic investigations of TOTM-plasticized EPDM, especially from the perspective of molecular structure regulation and sealing-related mechanical performance, remain limited. In this work, TOTM/EPDM systems with different TOTM contents were constructed and investigated by combining molecular dynamics simulations with experimental tests. Fractional free volume, mean square displacement, radial distribution function, coordination number, radius of gyration, and

simulated mechanical response were analyzed to reveal the effect of TOTM on the microstructure and segmental motion of EPDM. Experimental tensile, hardness, and stress relaxation tests were further conducted to validate the simulation results and evaluate the sealing-related mechanical performance. This study aims to clarify the structure–property relationship of TOTM-plasticized EPDM and provide a theoretical basis for optimizing EPDM-based sealing materials for long-term compressive service.

2 Materials and Methods

2.1 TOTM/EPDM Formulation Design

This study used EPDM as the matrix and TOTM as the plasticizer. Seven formulations with different plasticizer contents of 0, 5, 10, 15, 20, 25, and 30 wt% were designed. To highlight the plasticizing effect of TOTM on the EPDM matrix and minimize interference from other factors, the experimental system contained only EPDM and TOTM, without carbon black, silica, vulcanizing agents, accelerators, or other fillers. During sample preparation, the plate hot press was used only as a constant-temperature hot-compression molding device. Therefore, the obtained samples are more accurately defined as hot-pressed TOTM/EPDM specimens. This formulation design aimed to exclude, as far as possible, the complex effects of reinforcing fillers and crosslinked networks, thereby enabling a clearer investigation of the regulatory effects of TOTM content on EPDM segmental motion, microstructural evolution, and mechanical response.

Table 1. Formulation design of TOTM/EPDM specimens

Sample code	TOTM content / wt%	EPDM content / wt%	Description
E0	0	100	Neat EPDM control
E5	5	95	Low plasticizer content

E10	10	90	Low-to-moderate plasticizer content
E15	15	85	Candidate optimized formulation
E20	20	80	Candidate optimized formulation
E25	25	75	High plasticizer content
E30	30	70	Excessive plasticization risk group

2.2 Construction of Molecular Dynamics Models

EPDM chain models and TOTM molecular models were constructed using Materials Studio. The EPDM chain consisted of ethylene, propylene, and a small amount of non-conjugated diene structural units, while the TOTM molecule consisted of a trimellitate backbone and three octyl ester side chains. First, geometry optimization was performed for both the EPDM chains and TOTM molecules to eliminate unreasonable bond lengths, bond angles, and local high-energy configurations, thereby providing stable initial molecular structures for subsequent amorphous model construction.

During model construction, amorphous periodic models were built using the Amorphous Cell module based on the Monte Carlo random packing method according to the different TOTM/EPDM mass ratios listed in Table 1. Seven systems with mass ratios of 0/100, 5/95, 10/90, 15/85, 20/80, 25/75, and 30/70 were constructed to simulate the effects of different TOTM contents on the microstructure and segmental motion behavior of EPDM. The construction workflow of the TOTM/EPDM molecular models and the subsequent simulation analysis procedure are shown in Figure 1, including molecular structure construction, amorphous model generation, geometry optimization, annealing treatment, molecular dynamics equilibration, and extraction of microstructural parameters.

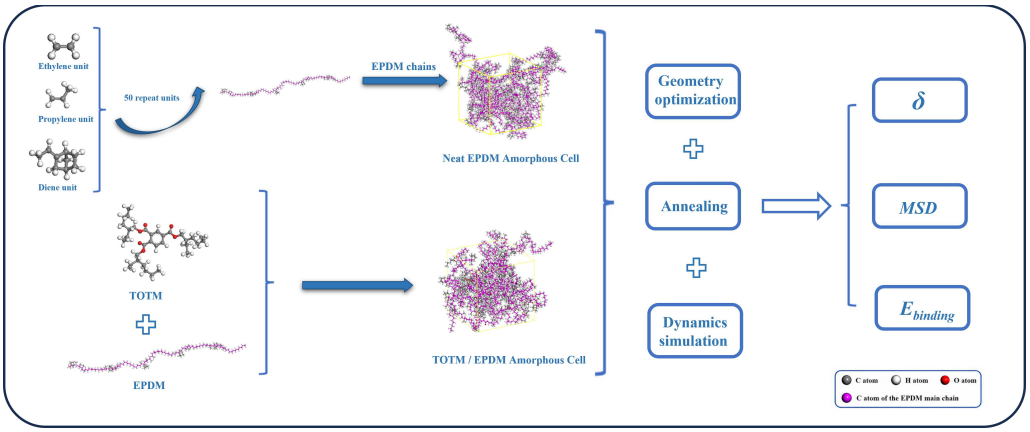


Figure 1. Molecular structures of TOTM/EPDM and construction workflow of the amorphous models

To visually demonstrate the internal component distribution of the systems with different TOTM contents, Figure 2 presents the amorphous models of TOTM/EPDM systems with different TOTM mass fractions. As the TOTM content increases, the number of TOTM molecules in the system gradually increases, and these molecules are progressively distributed among the EPDM chains. At low TOTM contents, TOTM mainly fills the local voids between chains. At moderate contents, TOTM is relatively well distributed within the EPDM matrix, which is beneficial for regulating the interchain packing state. When the TOTM content further increases, the number of TOTM molecules in local regions becomes significantly higher, indicating a possible tendency toward local enrichment. These model configurations provide a structural basis for subsequent analyses of binding energy distribution, fractional free volume, mean square displacement, radial distribution function, and radius of gyration.

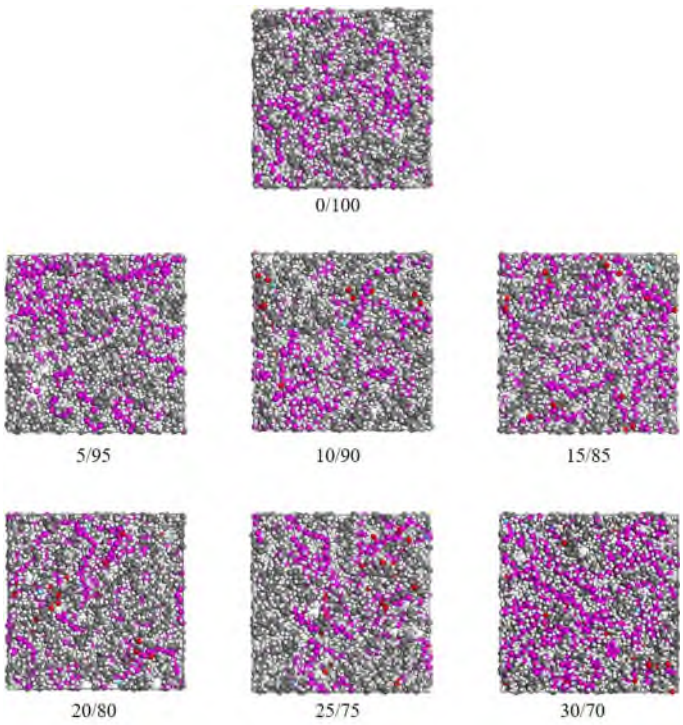


Figure 2. Equilibrated amorphous models of TOTM/EPDM systems with different TOTM contents.

To obtain relatively stable initial configurations and reduce the influence of random packing on the simulation results, the constructed amorphous models were sequentially subjected to geometry optimization, annealing treatment, and molecular dynamics equilibration. Geometry optimization was used to eliminate atomic overlaps and unreasonable local contacts in the initial models. Annealing treatment was performed to promote molecular chain conformational rearrangement and release internal stress. Subsequently, molecular dynamics equilibration under NVT and NPT ensembles was conducted to allow the temperature, density, and energy of the systems to gradually reach stable states. The equilibrated models were then used for subsequent analyses of fractional free volume, mean square displacement, radial distribution function, coordination number, radius of gyration, binding energy, and mechanical properties.

The COMPASS III force field was used to describe the bonded and non-bonded interactions in the molecular simulation. Electrostatic interactions were treated using the Ewald method, while van der Waals interactions were calculated using the atom-based method with a cutoff radius of 12.5 Å. The initial density of the models was set to 0.86 g/cm³, the simulation temperature was 298 K, and the pressure was 1 atm. Three-dimensional periodic boundary conditions were applied to represent bulk amorphous materials. To improve the statistical reliability of the simulation results, multiple independent models with different random seeds were constructed for each formulation, and the calculated results after equilibration were averaged. The detailed molecular dynamics simulation parameters are listed in Table 2.

Table 2. Molecular dynamics simulation parameter settings

Item	Parameter setting	Description
Software and modules	Materials Studio; Visualizer, Amorphous Cell, Forcite	Used for model construction, amorphous cell packing, and molecular dynamics simulations
Force field	COMPASS III	Suitable for polymer and organic molecular systems
Boundary conditions	Three-dimensional periodic boundary conditions	Used to simulate bulk amorphous materials
Initial density	0.86 g/cm³	Close to the common density range of EPDM rubber
Temperature and pressure	298 K, 1 atm	Used for room-temperature property calculations
van der Waals interactions	Atom-based method, cutoff radius of 12.5 Å	Used for non-bonded interaction calculations
Electrostatic interactions	Ewald method	Used for long-range electrostatic interactions
Geometry optimization	Smart algorithm; energy convergence tolerance: 1×10^{-4} kcal/mol	Used to eliminate atomic overlaps and unreasonable configurations
Annealing treatment	298→500→298 K; 5 cycles; NPT ensemble	Used to release internal stress and promote conformational rearrangement
Equilibration procedure	NVT 200 ps + NPT 500 ps + NVT 300 ps	Used to obtain stable density and energy states
Molecular dynamics time step	1 fs	Common time step for organic polymer systems
Data sampling	500 ps trajectory after equilibration	Used for statistical analysis of FFV, MSD, RDF, coordination number, and R_g

2.3 Molecular Simulation Analysis Methods

To quantitatively analyze the effects of TOTM on the microstructure, segmental motion, and mechanical response of EPDM, fractional free volume (FFV), mean square displacement (MSD), radial distribution function (RDF), coordination number, radius of gyration (R_g), and simulated mechanical parameters were selected as the main evaluation indicators. These parameters were used to characterize interchain free space, segmental mobility, local spatial distribution, effective contact, chain conformational changes, and the stiffness response of the system, respectively[29–32].

The fractional free volume was used to describe the proportion of unoccupied space in the system that is available for segmental motion and was calculated as follows:

$$\mathrm{FFV} = \frac{V_{\mathrm{cell}} - V_{\mathrm{occ}}}{V_{\mathrm{cell}}} \times 100\% \tag{1}$$

The mean square displacement was used to evaluate the segmental mobility within the simulation time scale, and is expressed as follows:

$$\mathrm{MSD}(t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle \tag{2}$$

The radial distribution function was used to describe the spatial proximity distribution between different atoms or groups, and can be expressed as follows:

$$g_{AB}(r) = \frac{1}{4\pi r^2 \rho_B N_A} \left\langle \sum_{i \in A} \sum_{j \in B} \delta(r - r_{ij}) \right\rangle \tag{3}$$

By further integrating the RDF, the average number of neighboring target particles within a given cutoff radius can be obtained, namely the coordination number:

$$N_{AB}(r_c) = 4\pi\rho_B \int_0^{r_c} g_{AB}(r) r^2 \, dr \tag{4}$$

The radius of gyration was used to characterize the spatial extension of EPDM molecular chains relative to their center of mass, and was calculated as follows:

$$R_g = \left(\frac{\sum_i m_i \left| \mathbf{r}_i - \mathbf{r}_{\mathrm{cm}} \right|^2}{\sum_i m_i} \right)^{1/2} \tag{5}$$

where V_{cell} and V_{occ} represent the total volume of the simulation cell and the occupied molecular volume, respectively; N is the number of atoms or segments included in the statistical analysis; $\mathbf{r}_i(t)$and $\mathbf{r}_i(0)$denote the positions of the i-th statistical object at time $t$and at the initial time, respectively; $A$and Brepresent the two types of atoms or groups selected for RDF analysis; $\rho_B$is the number density of type-B particles; $r_{ij}$is the distance between particles $i$and j; $r_c$is usually taken as the first minimum after the first peak of the RDF curve; $m_i$is the mass of the i-th atom; $\mathbf{r}_{\mathrm{cm}}$ is the center-of-mass position of the molecular chain; and the angle brackets $\langle\,\rangle$ denote averaging over the simulation trajectory or statistical objects.

In terms of simulated mechanical properties, the bulk modulus and shear modulus are denoted by $K$and G, respectively, and are used to characterize the stiffness and deformation resistance of the TOTM/EPDM system. In this work, elastic constants were calculated using the Forcite Mechanical Properties module, and the corresponding equivalent mechanical parameters were obtained through the built-in method of the software. Meanwhile, uniaxial tensile simulations were conducted to obtain the molecular simulation stress–strain curves, where stress and strain are denoted by $\sigma$and ε, respectively. These curves were used to compare the relative mechanical responses and softening trends of systems with different TOTM contents. It should be noted that the loading rate in molecular dynamics simulations is much higher than that under macroscopic experimental testing conditions, and the model size is far smaller than that of actual specimens.

Therefore, the simulated stress–strain curves were mainly used for trend comparison among different formulations rather than for directly replacing macroscopic experimental strength data.

2.4 Experimental Preparation and Testing Methods

EPDM and TOTM were weighed according to the formulations listed in Table 1. First, raw EPDM rubber was added to an internal mixer and plasticated at 115 °C for 5 min to improve the processing flowability of the rubber matrix. Subsequently, TOTM was added in batches, and mixing was continued for 10 min to ensure sufficient dispersion of the plasticizer within the EPDM matrix. After mixing, the compounded rubber was removed and placed into a molding die. A plate hot press was used as a constant-temperature hot-compression molding device, and the samples were molded at 165 °C and 10 MPa for 20 min. After demolding, TOTM/EPDM sheets were obtained. Figure 3 shows the mixing and hot-pressing equipment used in this study, where Figure 3(a) shows the internal mixer and Figure 3(b) shows the hot-pressing machine.



Figure 3. TOTM/EPDM specimen preparation equipment: (a) internal mixer; (b) hot-press molding machine.

To meet the requirements of different performance tests, the hot-pressed TOTM/EPDM sheets were further cut or prepared into specimens with corresponding geometries. Dumbbell-shaped specimens were used for tensile testing, while cylindrical specimens were used for compression set and stress relaxation tests. Figure 4 shows the prepared rubber test specimens and the main testing equipment, where Figure 4(a) shows the dumbbell-shaped tensile specimens and cylindrical compression specimens, Figure 4(b) shows the tensile testing machine, and Figure 4(c) shows the compression testing equipment. The overall specimen preparation and performance testing procedure is shown in Figure 5, including raw material weighing, mixing, discharge and transfer, hot-press molding, specimen preparation, and performance testing.



Figure 4. TOTM/EPDM specimens and performance testing equipment: (a) rubber test specimens; (b) tensile testing machine; (c) compression testing equipment.

Tensile properties were measured using a universal testing machine to obtain the experimental stress–strain curves, tensile strength, and elongation at break, which were used to evaluate the load-bearing capacity and large-deformation adaptability of the TOTM/EPDM systems. Hardness was measured using a Shore A durometer to characterize the resistance of the material to local indentation. Compression set tests were conducted under specified compression ratio, temperature, and time conditions to evaluate the deformation recovery capability of the material after long-term compression. Stress relaxation tests were performed by recording the stress decay over time under constant compressive deformation, which was used to characterize the sealing pressure retention capability of the material during compressive service. The correspondence between different testing items and the performance requirements of fuel cell sealing gaskets is listed in Table 3.

Table 3. Correlation between experimental testing items and fuel cell sealing performance

Testing item	Output indicator	Material significance	Relationship with sealing gasket performance
Tensile test	Stress–strain curve; elongation at break	Load-bearing capacity and ductility	Reflects adaptability to assembly deformation
Hardness test	Shore A hardness	Resistance to local indentation	Affects initial conformity and support capability
Compression set	Permanent deformation rate	Recovery ability after compression	Determines long-term sealing pressure retention
Stress relaxation	Stress retention rate	Viscoelastic pressure decay	Directly related to long-term leakage risk
Simulation/experiment comparison	Trend consistency	Mechanism validation	Supports formulation optimization

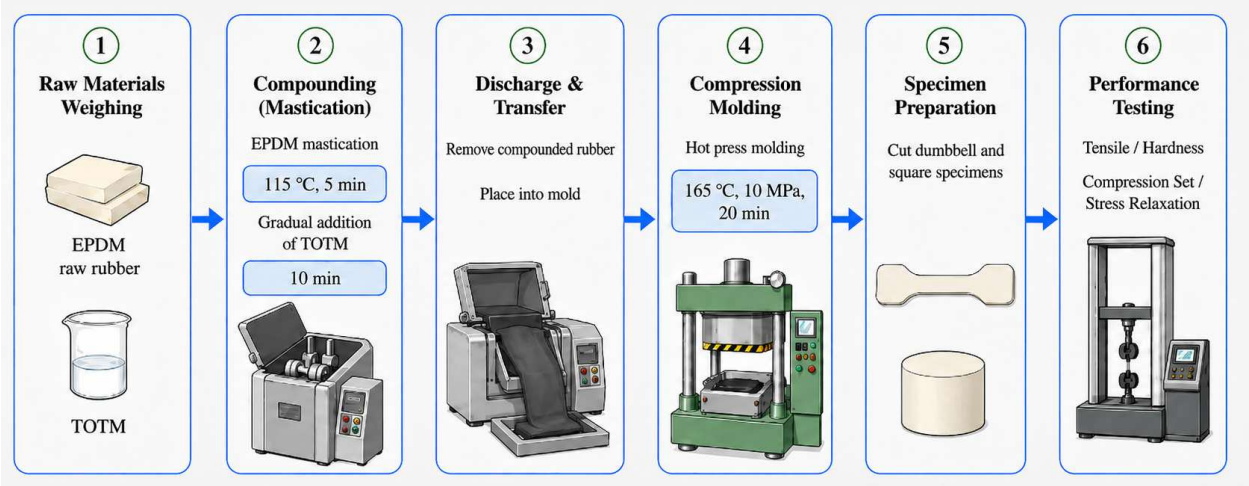


Figure 5. Schematic illustration of the preparation process of TOTM/EPDM specimens.

3 Results and Discussion

This section is organized according to the logical sequence of "model reliability validation–microstructural and segmental motion analysis–simulated mechanical response–experimental performance verification–sealing service correlation", thereby avoiding isolated discussion of individual simulation indicators. By correlating microscopic parameters, including FFV, MSD, RDF/coordination number, and R_g, with macroscopic properties such as modulus, hardness, elongation at break, and stress relaxation, the relationship between TOTM-regulated EPDM structure and the application performance of fuel cell sealing gaskets is established.

3.1 Equilibration Validation of the Molecular Dynamics Models

Before calculating the fractional free volume, segmental mobility, and mechanical properties, it was necessary to verify whether the constructed TOTM/EPDM amorphous periodic models had reached a stable state. In this study, the initial models were relaxed through a combined procedure of geometry optimization, annealing treatment, and molecular dynamics equilibration to eliminate atomic overlaps, unreasonable contacts, and local high-energy configurations that may arise during

random packing[33]. After geometry optimization, the unreasonable structures within the systems were preliminarily removed. Subsequently, annealing treatment was performed to promote molecular chain conformational rearrangement and further release internal stress. Finally, molecular dynamics equilibration was conducted under NVT and NPT ensembles to allow the temperature, energy, and density of the systems to gradually reach stable states.

Taking the 15/85 TOTM/EPDM system as an example, the variations in temperature and energy with simulation time are shown in Figure 6. As shown in Figure 6(a), the system temperature exhibits certain fluctuations at the initial stage of the simulation, which can be attributed to the relaxation of the initial configuration and conformational adjustment of molecular chains. With increasing simulation time, the magnitude of temperature fluctuation gradually decreases and eventually stabilizes around 298 K, indicating that the system reaches a stable thermal equilibrium state. Figure 6(b) shows that the total energy, non-bonded energy, kinetic energy, and potential energy of the system change rapidly at the initial stage and then gradually become stable, without continuous drift. This indicates that the internal interactions and conformational distribution of the system have basically reached equilibrium[34].

In summary, after geometry optimization, annealing treatment, and molecular dynamics equilibration, the temperature and energy of the TOTM/EPDM amorphous models reach stable states, indicating that the constructed models have good equilibration and reliability. Therefore, the equilibrated models can be used for subsequent calculations of FFV, MSD, RDF, coordination number, R_g, and mechanical properties.

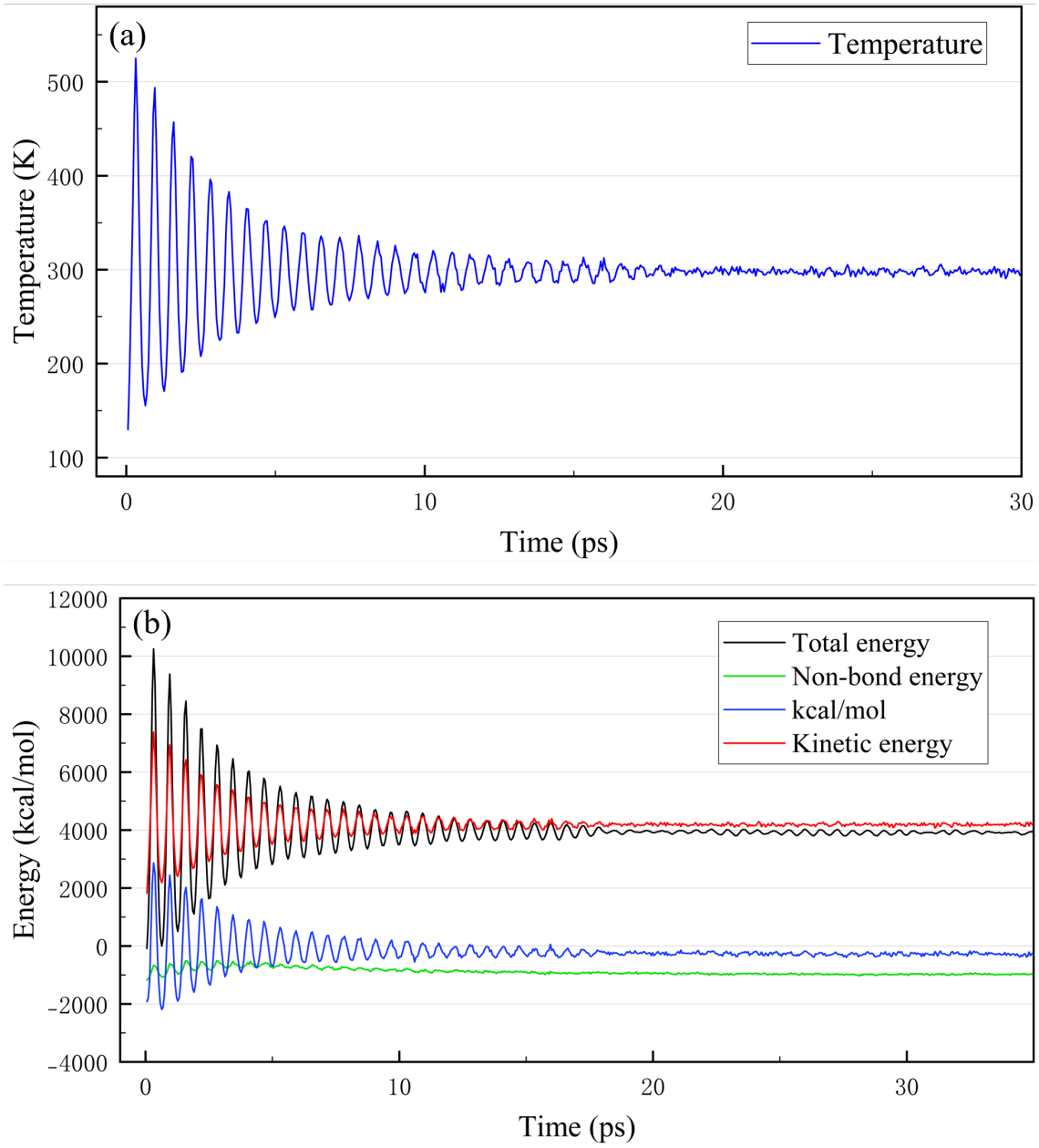


Figure 6. Molecular dynamics equilibration validation curves of the 15/85 TOTM/EPDM system: (a) temperature variation with time; (b) energy variation with time.

3.2 Effect of TOTM on the Microstructure and Segmental Motion of EPDM

After TOTM enters the interchain regions of EPDM, it can alter the local interactions between molecular chains, the interchain packing state, and the available free space, thereby affecting segmental mobility and conformational stability[23]. To reveal the regulation mechanism of

TOTM content on the microstructure of EPDM, the binding energy distribution, fractional free volume (FFV), mean square displacement (MSD), radial distribution function (RDF), coordination number, and radius of gyration (R_g) were comprehensively analyzed in this section.

Figure 7 shows the binding energy distributions among different components in the TOTM/EPDM system. Here, Ebs, Ebb, and Ess represent the interaction energy distributions between EPDM and TOTM, between EPDM and EPDM, and between TOTM and TOTM, respectively. It can be observed that the three distribution curves are mainly located in the negative energy region, indicating that attractive interactions dominate within the system. The Ebs curve suggests that a certain affinity exists between TOTM molecules and EPDM segments, indicating that TOTM can insert into the interchain regions of EPDM and form effective local contacts rather than simply existing as freely dispersed molecules in the system. The peak position of the Ebb curve is generally shifted toward the lower-energy region, suggesting that the original interactions among EPDM segments remain an important basis for maintaining the structural stability of the matrix. Meanwhile, the Ess curve also exhibits an obvious negative-energy distribution, indicating that attractive interactions also exist among TOTM molecules. This implies that, at relatively high TOTM contents, some TOTM molecules may be more inclined to undergo local enrichment or self-aggregation rather than remaining uniformly dispersed around EPDM segments. Therefore, from an energetic perspective, the binding energy distribution results indicate that an appropriate amount of TOTM is beneficial for forming a reasonable local interaction structure with EPDM, whereas excessive TOTM may cause local enrichment and reduce its effective regulation of EPDM chain packing and segmental motion.

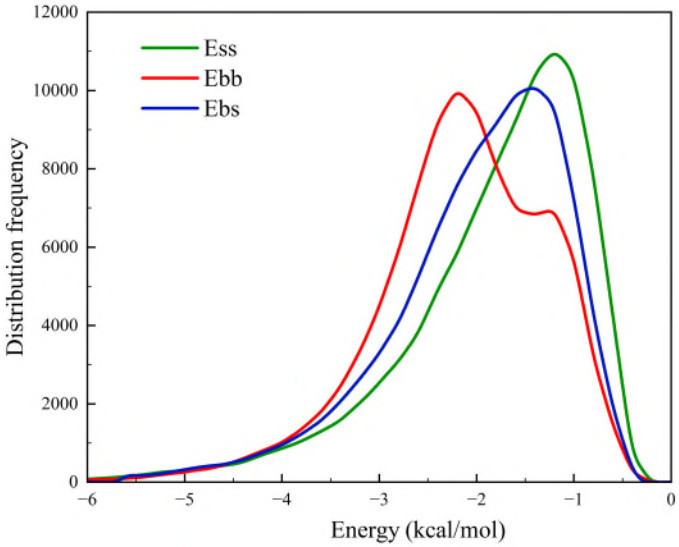


Figure 7. Binding energy distribution among different components in the TOTM/EPDM system.

Figure 8 presents the FFV and free volume visualization results of the TOTM/EPDM systems with different TOTM contents. The FFV does not increase monotonically with increasing TOTM content, but instead shows a trend of first decreasing and then slightly recovering. The FFV of the neat EPDM system is 15.3%, which decreases to 13.5% when the TOTM content increases to 15 wt%. Subsequently, the FFV slightly increases within the range of 20–30 wt% and remains at approximately 13.7%–14.0%. This result indicates that, at low to moderate TOTM contents, TOTM molecules preferentially fill the original microvoids between EPDM chains, leading to a more compact local packing structure and thus a decrease in FFV. When the TOTM content further increases, the plasticizing effect gradually becomes more pronounced, and the interchain spacing and local available motion space partially recover, resulting in a slight increase in FFV. This suggests that the effect of TOTM on the free volume of EPDM is not a simple spatial expansion, but rather the combined result of interchain void filling and plasticization-induced relaxation. In

combination with Figure 7, this phenomenon can be further understood as follows: appropriate effective interactions between TOTM and EPDM facilitate the insertion of TOTM into the interchain regions and improve local packing, whereas the self-aggregation tendency induced by excessive TOTM may weaken this compacting effect.

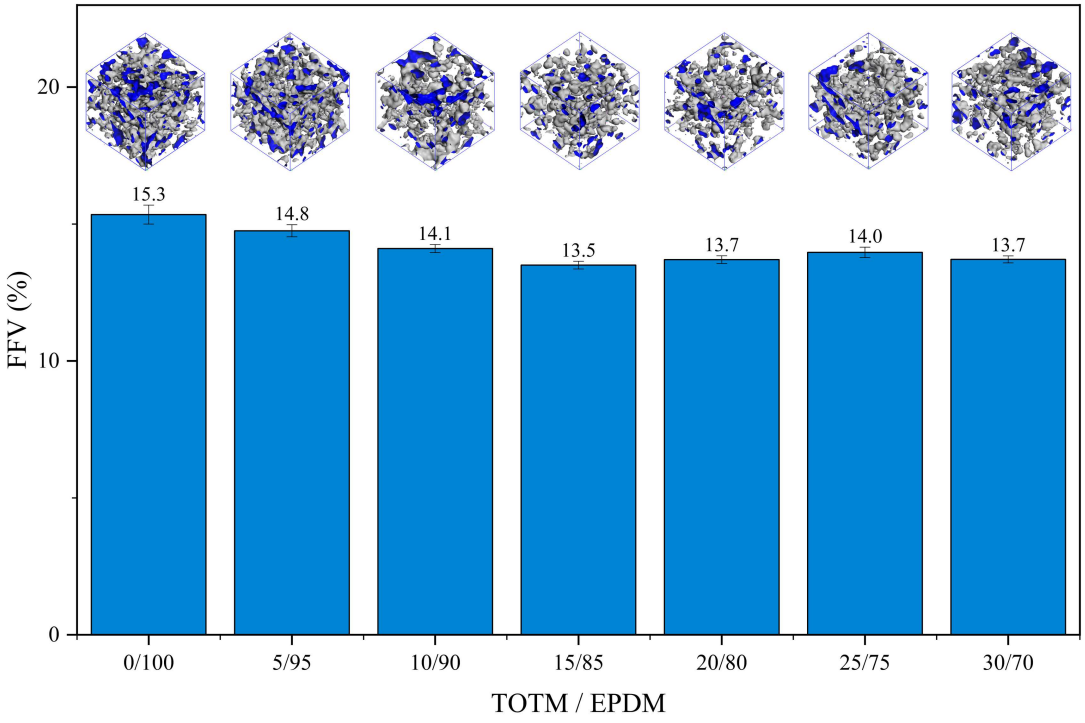


Figure 8. Fractional free volume and free volume distribution of TOTM/EPDM systems with different TOTM contents

The variation in segmental mobility is further reflected by the MSD results, as shown in Figure 9(a). Compared with neat EPDM, the MSD curves of all TOTM-containing systems shift upward overall, indicating that TOTM can weaken the constraints among EPDM segments and enhance segmental mobility. Among them, the systems with moderate TOTM contents exhibit relatively higher MSD levels, suggesting that an appropriate amount of TOTM provides a more favorable motion environment for chain conformational adjustment. For fuel cell sealing gaskets, moderately

enhanced segmental mobility is beneficial for the material to adapt to the microscopic roughness of bipolar plates or flow-field plates during compression assembly, thereby improving interfacial conformity[35]. However, higher segmental mobility is not always preferable. If the TOTM content is too high, the interchain constraints may be excessively weakened, which may reduce the dimensional stability and stress retention capability of the material. Therefore, the MSD results should be further discussed together with subsequent macroscopic properties, such as modulus, hardness, and stress relaxation.

Figure 9. (b) shows the RDF and coordination number analysis results of the TOTM/EPDM systems. The coordination number can be used to characterize the spatial proximity and effective contact state between TOTM molecules and EPDM segments. With increasing TOTM content, the coordination number first increases and then decreases, reaching a relatively high level near 15 wt%. This indicates that, at this content, TOTM can be sufficiently distributed in the interchain regions of EPDM and form more effective local contacts with EPDM segments. When the TOTM content continues to increase, the coordination number does not further increase, suggesting that the number of effective TOTM contacts around unit EPDM segments does not increase synchronously with the total amount of plasticizer. This result is consistent with the binding energy distribution shown in Figure 7; that is, at higher TOTM contents, enhanced TOTM–TOTM interactions cause some TOTM molecules to be more prone to local enrichment rather than further uniform dispersion around EPDM segments, thereby reducing their effective regulation of segmental motion and chain packing.

Figure 9(c) shows the time-dependent variation in the radius of gyration of EPDM chains with different TOTM contents. R_g reflects the spatial extension of polymer chains relative to their center of mass and can be used to evaluate the extended or coiled state of chain conformations[36].

The neat EPDM system exhibits a relatively low R_g, indicating that the molecular chains are strongly restricted by interchain interactions and entanglements, resulting in a more contracted conformation. After the addition of TOTM, R_g increases overall, suggesting that the plasticizer weakens the interactions among chain segments and promotes a more extended EPDM chain conformation. At moderate TOTM contents, R_g remains at a relatively high and stable level, indicating that the chains possess good mobility while maintaining a certain degree of conformational stability. In contrast, at excessively high TOTM contents, the fluctuation of R_g becomes more pronounced or shows a decreasing tendency, implying that local chain coiling or conformational instability may occur under over-plasticized conditions. This behavior corresponds to the subsequent reduction in mechanical support capability and the increased risk of stress relaxation.

Overall, the results from Figure 7 to Figure 9 demonstrate that the regulation of the EPDM microstructure by TOTM is strongly content-dependent. An appropriate amount of TOTM can form reasonable local interactions with EPDM segments, enter the interchain regions, and regulate the interchain free space, thereby enhancing segmental mobility, increasing effective local contacts, and maintaining good conformational stability. In contrast, excessive TOTM may lead to local enrichment and excessive weakening of interchain constraints, resulting in the risk of over-softening and decreased conformational stability. Therefore, a moderate TOTM content is more favorable for achieving a balance between enhanced segmental mobility and structural stability, providing a microscopic basis for the subsequent optimization of macroscopic mechanical properties and sealing service performance.

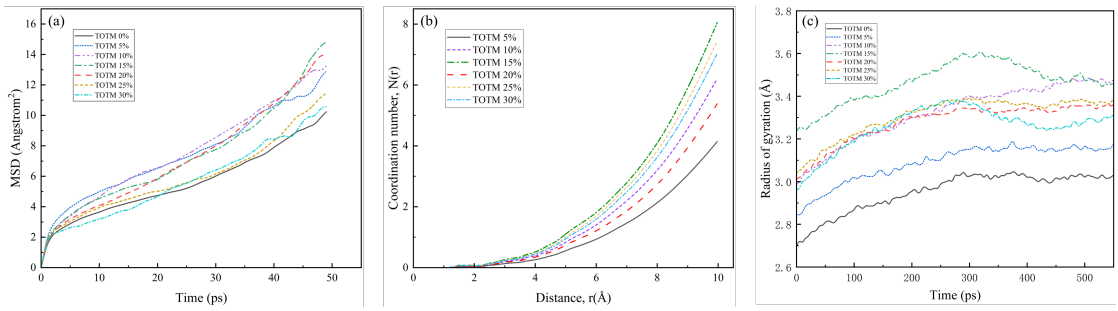


Figure 9. MSD, RDF/coordination number, and R_g analysis results of the TOTM/EPDM system

3.3 Effect of TOTM on the Simulated Mechanical Response of EPDM

Changes in microstructure and segmental mobility are further reflected in the mechanical response of the material. Figure 10 presents the bulk modulus, shear modulus, and molecular simulation stress–strain curves of the TOTM/EPDM systems with different TOTM contents. By comparing the mechanical parameters of different formulations, the effects of TOTM on the stiffness, deformation resistance, and flexibility of the EPDM system can be further analyzed.

As shown in Figure 10(a), with increasing TOTM content, the bulk modulus of the TOTM/EPDM system shows an overall decreasing trend, decreasing from approximately 1.91 GPa for neat EPDM to approximately 1.57–1.58 GPa for the systems with high TOTM contents. The decrease in bulk modulus indicates that the resistance of the system to compressive volumetric deformation is weakened, and the overall rigidity of the material is reduced[37, 38]. This is mainly because TOTM molecules enter the interchain regions of EPDM, weakening the direct interactions between molecular chains and the constraints among chain segments, thereby making the system more prone to deformation under external loading.

The shear modulus exhibits a nonmonotonic variation. As the TOTM content increases from 0 wt% to the moderate content range, the shear modulus increases to a certain extent. However, when the TOTM content further increases, the shear modulus gradually decreases. This indicates

that, at low to moderate contents, TOTM may preferentially fill the interchain voids of EPDM and improve the local packing state, allowing the system to maintain a certain deformation resistance under shear deformation. In contrast, at high TOTM contents, the plasticization-induced softening effect becomes dominant; segmental mobility is enhanced and interchain constraints are weakened, resulting in a decrease in shear modulus. This variation trend is consistent with the aforementioned FFV and local contact analyses, suggesting that the effect of TOTM on the mechanical properties of EPDM is not a simple linear softening process, but rather involves a competition between local packing densification and plasticization-induced relaxation.

Figure 10(b) shows the molecular simulation stress–strain curves of the systems with different TOTM contents. With increasing TOTM content, the curves shift overall toward the lower-stress region, and the stress at the same strain gradually decreases. This indicates that the addition of TOTM reduces the deformation resistance of the EPDM system, making the material more susceptible to tensile deformation and improving its flexibility. For fuel cell sealing gaskets, a moderate reduction in stress level and modulus is beneficial for enabling the gasket to undergo the necessary deformation under a lower assembly load, thereby allowing it to better conform to the microscopic roughness of bipolar plates or flow-field plates and improving the initial interfacial conformity[14].

It should be noted that the loading rate in molecular dynamics simulations is much higher than that under macroscopic experimental testing conditions, and the model size is much smaller than that of actual specimens.[39] Therefore, the simulated stress–strain curves are mainly used to compare the relative mechanical responses and softening trends among different formulations, rather than to establish a direct numerical correspondence with the experimental stress–strain curves. Overall, the modulus and simulated stress–strain results indicate that TOTM can

effectively reduce the stiffness of the EPDM system and improve material flexibility. However, excessive TOTM may also weaken the mechanical support capability of the system, providing a simulation basis for subsequent analyses of experimental mechanical properties and long-term sealing stability.

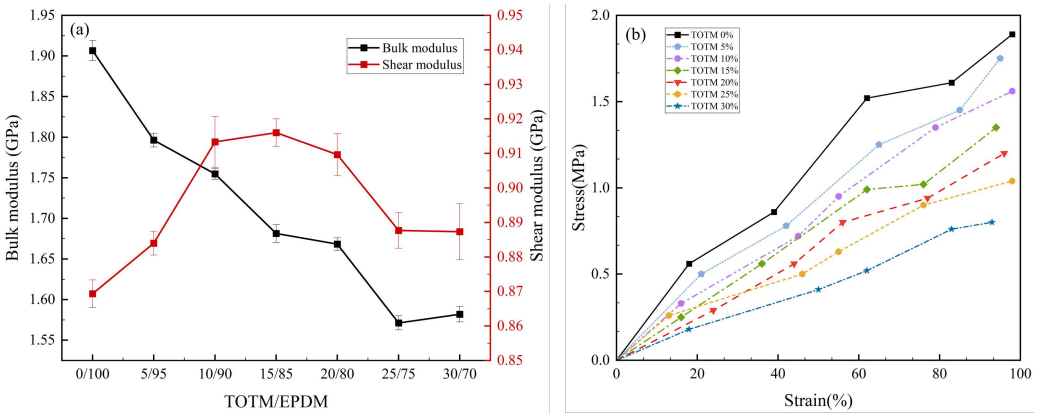


Figure 10. Simulated mechanical properties of TOTM/EPDM systems with different TOTM contents: (a) bulk modulus and shear modulus; (b) molecular simulation stress–strain curves.

3.4 Effect of TOTM on the Experimental Mechanical Properties and Compressive Service Performance of EPDM

The experimental mechanical properties are shown in Figure 11. With increasing TOTM content, the stress–strain curves of the TOTM/EPDM specimens shift overall toward the lower-stress region, and the corresponding stress at the same strain gradually decreases. This indicates that TOTM can weaken the interactions among EPDM segments, reduce material rigidity, and improve flexibility. This trend is generally consistent with the decrease in modulus and the downward shift of the simulated stress–strain curves observed in the molecular simulation results, confirming the evident plasticizing and softening effect of TOTM on the EPDM system.

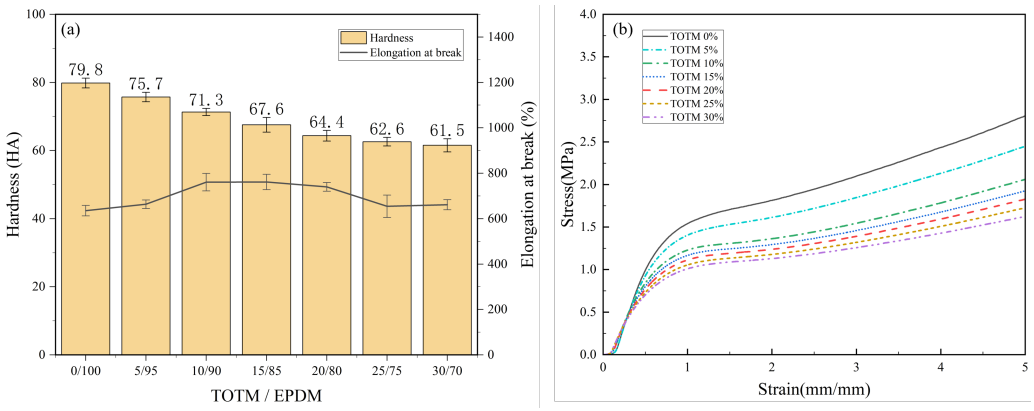


Figure 11. Experimental mechanical properties of TOTM/EPDM specimens with different TOTM contents: (a) hardness and elongation at break; (b) experimental stress–strain curves.

The hardness test results further verify this trend. The Shore A hardness of the neat EPDM specimen is approximately 79.8 HA. As the TOTM content increases, the hardness gradually decreases, reaching approximately 61.5 HA at 30 wt% TOTM. The decrease in hardness indicates that the material exhibits reduced resistance to local indentation deformation, while also suggesting that it is more likely to undergo compressive deformation under a lower assembly load. For fuel cell sealing gaskets, a moderate reduction in hardness is beneficial for improving the conformity of the gasket to the microscopic roughness of bipolar plates or flow-field plates, thereby enhancing the initial interfacial contact. However, excessively low hardness may weaken the support capability under long-term compression and make the sealing contact pressure more prone to decay[40].

The elongation at break first increases and then decreases with increasing TOTM content. The elongation at break of the neat EPDM specimen is approximately 632.8%. After the addition of TOTM, the ductility of the material is significantly improved, with the 10 wt% TOTM system

reaching the highest value of approximately 768.3%. The 15 wt% TOTM system still maintains a relatively high value of approximately 757.8%. When the TOTM content further increases to 20–30 wt%, the elongation at break gradually decreases. This result suggests that an appropriate amount of TOTM can enhance the segmental mobility and tensile deformation capacity of EPDM, enabling the material to exhibit better deformation adaptability under external loading. In contrast, excessive TOTM may excessively weaken interchain constraints and reduce chain entanglement and structural support, thereby decreasing the stability of the material under large deformation.

Figure 12 shows the stress relaxation behavior of TOTM/EPDM specimens with different TOTM contents. Stress relaxation reflects the ability of a material to maintain sealing contact pressure under constant compressive deformation and is an important indicator for evaluating the long-term service reliability of fuel cell sealing gaskets[39, 41]. It can be observed that the stress of all specimens decreases rapidly at the initial loading stage, followed by a gradual reduction in the decay rate and eventual stabilization, showing typical viscoelastic relaxation behavior of rubber materials. Neat EPDM exhibits a relatively high initial stress but undergoes rapid stress decay over time, indicating a high initial support stiffness but limited long-term pressure retention capability. After the addition of TOTM, the initial rigidity of the material decreases; however, some TOTM-modified systems exhibit higher residual stress levels during long-term compression, suggesting that appropriate plasticization contributes to improved compressive deformation coordination and stress retention capability.

Stress relaxation performance should not be used as the sole criterion for judging the superiority of a formulation. A higher residual stress may originate from better viscoelastic recovery, but it may also be related to the initial stiffness, compression state, and deformation mode of the material. Although excessive TOTM may show relatively high stress retention during

certain time intervals, its over-softening effect, enhanced segmental slippage, and potential plasticizer migration risk may still affect long-term sealing stability. Therefore, the evaluation of fuel cell sealing gasket formulations should comprehensively consider hardness, modulus, elongation at break, compression set, and stress relaxation results, rather than determining the optimal content based on a single indicator.

Overall, the experimental results show that the effect of TOTM on EPDM is not a simple linear softening process, but rather involves a competition between improved flexibility and retained structural support. An appropriate amount of TOTM can reduce hardness and stress level while improving material flexibility, ductility, and interfacial conformity. However, excessive TOTM may weaken interchain support and increase the risks of irreversible deformation and long-term sealing pressure decay. Based on the hardness, elongation at break, and stress relaxation results, the specimens containing 10–20 wt% TOTM exhibit relatively good overall performance, with the formulation near 15 wt% showing a better balance among flexibility, deformation adaptability, and long-term compressive service stability.

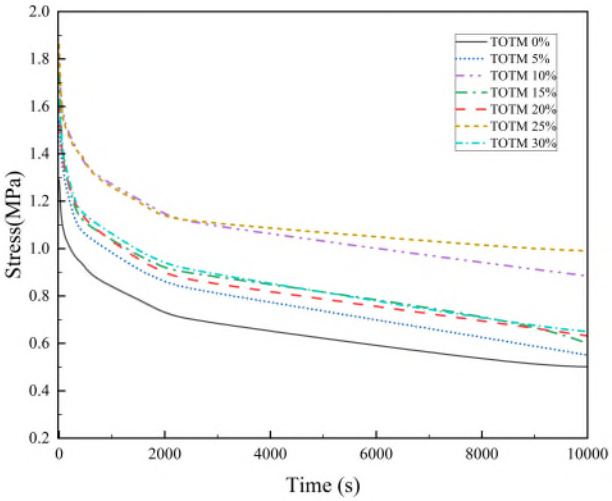


Figure 12. Stress relaxation curves of TOTM/EPDM specimens with different TOTM contents.

4 Structure–Property Correlation for Sealing-Related Performance

Elastomeric sealing materials used in long-term compressive service are required to maintain interfacial conformity, compression recovery, and stress retention. Fuel cell sealing gaskets represent a typical demanding application scenario, where the gasket must conform to microscopic roughness while maintaining stable contact pressure under compression, temperature fluctuations, and service media[42]. Therefore, the evaluation of fuel cell sealing gasket materials should not rely solely on a single indicator, such as hardness, modulus, or elongation at break, but should comprehensively consider interfacial conformity, compression recovery, stress retention, and long-term sealing stability.

Based on the molecular simulation and experimental results, the performance evolution of the TOTM/EPDM system can be summarized as a progressive process of "molecular structural regulation–segmental motion variation–macroscopic mechanical response–sealing service performance". After TOTM enters the interchain regions of EPDM, it first alters the chain packing state and local spatial structure, resulting in content-dependent changes in microscopic indicators such as FFV, MSD, RDF/coordination number, and R_g. Subsequently, these microstructural changes are further reflected in macroscopic properties, including reduced modulus, lower stress at the same strain, decreased hardness, and an initial increase followed by a decrease in elongation at break. These results indicate that the effect of TOTM on EPDM is not a simple linear softening process, but rather involves a balance among enhanced segmental mobility, retained structural compactness, and mechanical support capability.

From the perspective of initial sealing performance, a moderate reduction in hardness and modulus is beneficial for enabling the gasket to undergo the necessary compressive deformation under a lower assembly load, thereby more effectively filling the microscopic gaps on the surfaces

of bipolar plates or flow-field plates, increasing the real contact area, and reducing the possibility of initial micro-leakage channel formation[42, 43]. The FFV results show that, after the addition of TOTM, the fractional free volume of the system first decreases and then slightly recovers, indicating that an appropriate amount of TOTM can regulate the interchain space while avoiding excessive loosening of the system. This is beneficial for achieving a balance between structural compactness and segmental flexibility. The MSD results further indicate that TOTM can enhance the segmental mobility of EPDM, allowing the material to undergo conformational adjustment more readily under external loading, which corresponds to the downward shift of the experimental stress–strain curves, the decrease in hardness, and the improvement in flexibility. The RDF/coordination number and R_g results indicate that, at moderate TOTM contents, sufficient effective contact exists between TOTM molecules and EPDM segments, and the chain conformations remain relatively stable. These features provide a microscopic basis for the interfacial adaptive deformation of gaskets during compressive assembly.

From the perspective of long-term sealing reliability, compression set and stress relaxation are more critical evaluation factors. If a gasket undergoes a large compression set under long-term constant compression, the sealing contact pressure may decrease due to insufficient recovery even when the initial sealing performance is satisfactory. If stress relaxation proceeds too rapidly, the contact pressure of the gasket under a fixed compression level will continuously decay, ultimately increasing the risk of hydrogen, air, or coolant leakage[44]. Therefore, the TOTM content should not be optimized solely to reduce hardness, decrease modulus, or enhance segmental mobility; instead, a balance should be achieved between improved flexibility and retained support capability. An appropriate amount of TOTM can improve deformation adaptability and interfacial conformity potential, whereas excessive TOTM may lead to local enrichment, weakened interchain constraints,

and over-softening, thereby reducing the support capability of the material and increasing the risks of compression set, stress relaxation, and long-term leakage.

Based on the above analysis, 15–20 wt% TOTM can be regarded as a candidate optimization range for TOTM/EPDM systems intended for sealing-related mechanical performance, especially for fuel-cell-gasket-related service conditions. Within this range, TOTM can effectively enhance segmental mobility, moderately reduce hardness and stress level, and still maintain good deformation adaptability and a certain degree of structural support. In particular, near 15 wt% TOTM, molecular simulation indicators such as RDF/coordination number, R_g, and MSD suggest that the system possesses sufficient local contact, a reasonable chain conformational state, and favorable segmental mobility. The macroscopic experimental results also show good flexibility, elongation at break, and stress retention potential. Therefore, a TOTM content close to 15 wt% is more likely to achieve a favorable balance among initial interfacial conformity, mechanical support capability, and long-term sealing stability.

Since the TOTM/EPDM system used in this study is a simplified hot-pressed system without the vulcanization system, reinforcing fillers, and other functional additives commonly used in practical sealing gasket formulations, the 15–20 wt% TOTM range should be regarded as a candidate optimization range rather than a final engineering formulation. Further verification of its engineering applicability is still required by incorporating complete vulcanization formulations, compression set tests, leakage rate measurements, medium aging tests, temperature cycling, and long-term durability evaluations. To further clarify the relationship among molecular simulation indicators, experimental properties, and sealing significance, the corresponding structure–property–sealing correlations are summarized in Table 4. In addition, to visually illustrate the transfer relationship among TOTM content, EPDM microstructure, macroscopic properties, and

sealing service behavior, a schematic illustration of the correlation mechanism between TOTM-plasticized EPDM and sealing-related performance is presented in Figure 13.

Table 4. Correspondence among molecular simulation indicators, experimental properties, and sealing significance

Indicator	Microscopic meaning	Experimental response	Sealing relevance
FFV	Free-volume regulation	Lower hardness; higher flexibility	Improves compactness–conformity balance
MSD	Segmental mobility	Lower stress; higher elongation	Enhances adaptation to rough interfaces
RDF/coordination number	TOTM–EPDM local contact	Lower modulus and hardness	Confirms effective plasticizer insertion
R_g	Chain conformation stability	Nonmonotonic elongation change	Supports deformation adaptability
Modulus/stress–strain	Relative stiffness response	Reduced stress and hardness	Improves conformity but may weaken support if excessive

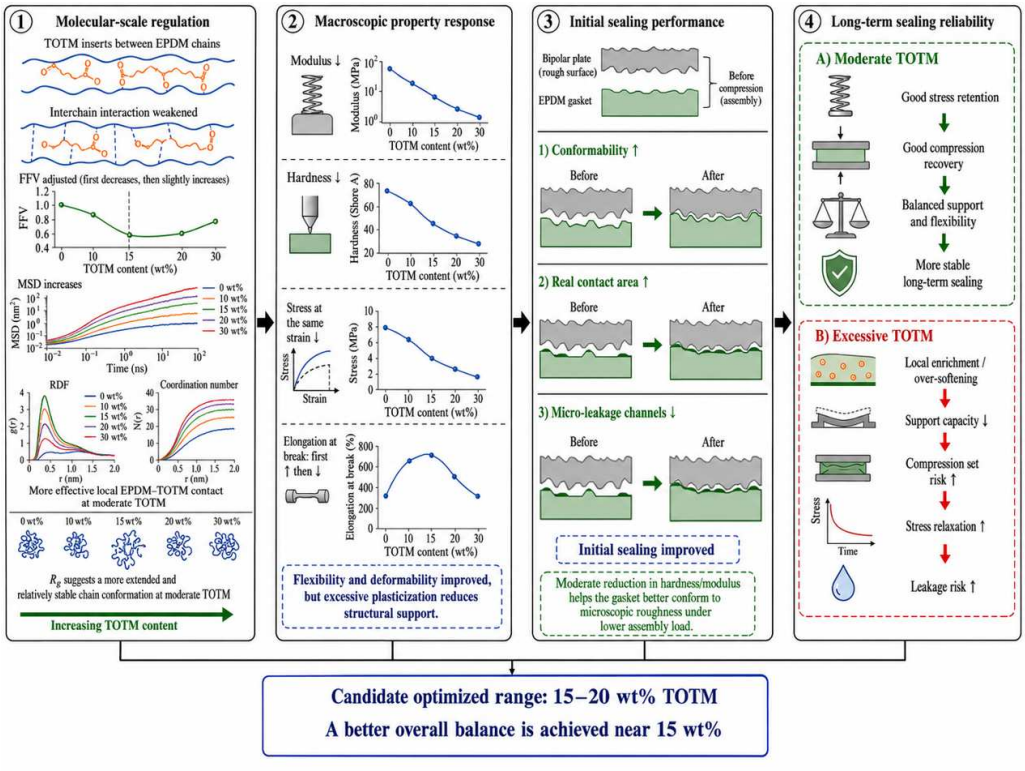


Figure 13. Schematic illustration of the structure–property–sealing performance correlation of TOTM-plasticized EPDM

5 Conclusions

In this study, a binary hot-pressed TOTM/EPDM system was investigated by combining molecular dynamics simulations with experimental tests. The effects of different TOTM contents on the microstructure, segmental motion, mechanical response, and fuel-cell-gasket-related service performance of EPDM were systematically analyzed. The main conclusions are as follows:

(1) TOTM can enter the interchain regions of EPDM and alter the local interactions, interchain packing state, and free volume distribution of the system. The binding energy distribution results indicate that a certain affinity exists between TOTM and EPDM, which facilitates the insertion of TOTM into the interchain regions of EPDM and the formation of effective local contacts. Meanwhile, attractive interactions also exist among TOTM molecules, suggesting that local

enrichment or self-aggregation may occur at high TOTM contents. The equilibrated amorphous models with different TOTM contents further show that an appropriate amount of TOTM can be relatively well distributed within the EPDM matrix, whereas excessive TOTM may reduce its effective regulation of the chain packing state.

(2) The regulation of the EPDM microstructure by TOTM exhibits obvious content dependence. The FFV results show that the fractional free volume of the system first decreases and then slightly recovers with increasing TOTM content, indicating that TOTM has both an interchain void-filling effect and a plasticization-induced relaxation effect on EPDM. The MSD, RDF/coordination number, and R_g results further demonstrate that systems with moderate TOTM contents exhibit improved segmental mobility, effective local contact, and conformational stability. In contrast, excessive TOTM may lead to weakened interchain constraints, local enrichment, and reduced conformational stability.

(3) Both molecular simulations and experimental tests confirm that TOTM can reduce the stiffness of the EPDM system and improve material flexibility. With increasing TOTM content, the bulk modulus of the TOTM/EPDM system decreases overall, and the simulated stress–strain curves shift toward the lower-stress region. Experimentally, the stress–strain curves of the TOTM/EPDM specimens also shift downward, and the Shore A hardness decreases from approximately 79.8 HA for neat EPDM to approximately 61.5 HA for the 30 wt% TOTM system. The elongation at break first increases and then decreases with increasing TOTM content, and remains relatively high within the range of 10–15 wt%. These results indicate that an appropriate amount of TOTM can improve the large-deformation adaptability of EPDM, whereas excessive TOTM weakens structural support.

(4) For sealing-related applications, especially fuel cell gasket service, the TOTM content should be balanced among initial interfacial conformity, mechanical support capability, and long-term sealing reliability. An appropriate amount of TOTM can reduce hardness and stress level, improve material flexibility and interfacial conformity potential, and enhance compressive deformation coordination. However, excessive TOTM may induce over-softening, enhanced segmental slippage, and reduced stress retention capability, thereby increasing the risk of long-term leakage. Based on the molecular simulation and experimental results, 15–20 wt% TOTM can be regarded as a candidate optimization range for TOTM/EPDM systems intended for sealing-related mechanical performance, especially for fuel-cell-gasket-related service conditions. In particular, the formulation near 15 wt% shows a better overall balance in terms of segmental mobility, local contact state, conformational stability, flexibility, and stress retention potential.

Since the TOTM/EPDM system investigated in this study is a simplified binary hot-pressed system without the vulcanization system, reinforcing fillers, and other functional additives commonly used in practical sealing gasket formulations, the proposed 15–20 wt% TOTM range should mainly serve as a guide for subsequent formulation design rather than as a final engineering formulation. Future work should further incorporate complete vulcanization formulations, reinforcing systems, compression set tests, medium aging, temperature cycling, leakage rate measurements, and long-term durability evaluation to verify its engineering applicability under fuel-cell-gasket-related service conditions.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Grant No. 52575584).

Author contributions Wanjia Sheng: Conceptualization, Methodology, Molecular dynamics simulation, Experimental investigation, Data curation, Visualization, Writing – original draft. Yanfeng Xing: Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review and editing. Fuyong Yang: Methodology, Experimental investigation, Data analysis. Juyong Cao: Experimental investigation, Data validation, Formal analysis. Ying Wang: Data analysis, Visualization, Writing – review and editing. Xiaobing Zhang: Supervision, Resources, Writing – review and editing. All authors have read and approved the final manuscript.

Conflict of interest The authors declare that they have no conflicts of interest related to this work.

REFERENCES

1. Debe MK, Schmoeckel A, Hendricks S, et al (2006) Durability aspects of nanostructured thin film catalysts for PEM fuel cells. ECS Trans 1:51–66.
2. Asmatulu R, Khan A, Adigoppula VK, Hwang G (2018) Enhanced transport properties of graphene-based, thin nafion® membrane for polymer electrolyte membrane fuel cells. Int J Energy Res 42:508–519.
3. Hooshyari K, Amini Horri B, Abdoli H, et al (2021) A review of recent developments and advanced applications of high-temperature polymer electrolyte membranes for PEM fuel cells. Energies 14:5440.
4. Garland N, Benjamin T, Kopasz J (2007) DOE fuel cell program: durability technical targets and testing protocols. ECS Trans 11:923–931.
5. Yuan H, Dai H, Ming P, et al (2022) Understanding dynamic behavior of proton exchange membrane fuel cell in the view of internal dynamics based on impedance. Chemical Engineering Journal 431:134035.
6. Liu L, Ma H, Khan M, Hsiao BS (2024) Recent Advances and Challenges in Anion Exchange Membranes Development/Application for Water Electrolysis: A Review. Membranes 14:85.
7. Shi D, Cai L, Zhang C, et al (2023) Fabrication methods, structure design and durability analysis of advanced sealing materials in proton exchange membrane fuel cells. Chemical Engineering Journal 454:139995.
8. Wei Y, Xing Y, Zhang X, et al (2024) A Review of Sealing Systems for Proton Exchange Membrane Fuel Cells. WEVJ 15:358. https://doi.org/10.3390/wevj15080358 H, Chen M, Wang H (2024) New insights into the performance and durability degradation mechanisms of PEMFCs caused by Cr3+ contaminant. Fuel 365:131253.
10. Kim J-W, Park HR, Choi WJ, et al (2026) Deciphering the long-term failure mechanism of the sealing framework in a proton exchange membrane fuel cell by assessing multi-stress degradation under accelerated simulated operating conditions. Chem Eng J 538:177005.
11. Li K, Zhang B, Yang Z, et al (2022) Degradation behaviors of silicone gel encapsulation material with moisture intrusion. Polymer Degradation and Stability 206:110197.
12. Li G, Zhu D, Jia W, Zhang F (2021) Analysis of the aging mechanism and life evaluation of elastomers in simulated proton exchange membrane fuel cell environments. e-Polymers 21:921–929.
13. Simon A, Pepin J, Berthier D, Méo S (2023) Degradation mechanism of FKM during thermo-oxidative aging from mechanical and network structure correlations. Polymer Degradation and Stability 208:110271.
14. Zhao J, Guo H, Xing Y, et al (2023) A review on the sealing structure and materials of fuel-cell stacks. Clean Energy 7:59–69.
15. Yang D, Tan Y, Li B, et al (2022) A Review of the Transition Region of Membrane Electrode Assembly of Proton Exchange Membrane Fuel Cells: Design, Degradation, and Mitigation. Membranes 12:306.
16. Chu T, Xie M, Yu Y, et al (2022) Experimental study of the influence of dynamic load cycle and operating parameters on the durability of PEMFC. Energy 239:122356.
17. Wu F, Chen B, Yan Y, et al (2018) Degradation of Silicone Rubbers as Sealing Materials for Proton Exchange Membrane Fuel Cells under Temperature Cycling. Polymers 10:522.
18. Tan J, Chao YJ, Wang H, et al (2009) Chemical and mechanical stability of EPDM in a PEM fuel cell environment. Polym Degrad Stab 94:2072–2078.

19. Cui T, Chao YJ, Van Zee JW (2012) Stress relaxation behavior of EPDM seals in polymer electrolyte membrane fuel cell environment. Int J Hydrogen Energy 37:13478–13483.
20. Shen L, Xia L, Han T, et al (2016) Improvement of hardness and compression set properties of EPDM seals with alternating multilayered structure for PEM fuel cells. Int J Hydrogen Energy 41:23164–23172.
21. Kusoglu A, Weber AZ (2017) New insights into perfluorinated sulfonic-acid ionomers. Chem Rev 117:987–1104.
22. Rahman M, Brazel C (2004) The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. Prog Polym Sci 29:1223–1248.
23. Li D, Panchal K, Vasudevan NK, et al (2022) Effects of molecular design parameters on plasticizer performance in poly(vinyl chloride): a comprehensive molecular simulation study. Chem Eng Sci 249:117334.
24. Nagorka R, Goral T, Scholz U, Meinecke S (2025) Release of high-molecular-weight plasticizers from PVC: mesocosm experiments under near-natural conditions. Environ Sci Eur 37:75.
25. Lai H, Wang Z, Wu P, et al (2012) Structure and diffusion behavior of trioctyl trimellitate (TOTM) in PVC film studied by ATR-IR spectroscopy. Ind Eng Chem Res 51:9365–9375.
26. Tang L, Chang X, Zhao Y (2023) Molecular simulation of the effect of dioctyl phthalate on the properties of nitrile rubber. Mater Today Commun 37:106983.
27. Wang Y, Yang Y, Tao M (2019) Understanding free volume characteristics of ethylene-propylene-diene monomer (EPDM) through molecular dynamics simulations. Materials 12:612.
28. He S, Zeng Z, Liu H, et al (2026) Multi-mechanism biomass-derived poly(tannic acid)-based antioxidant (PTRB) for enhanced the thermo-oxidative resistance of NBR: insights from experiments and molecular simulations. Polym Degrad Stab 245:111881.
29. Song S, Jiao F, Yang B, et al (2026) Mechanical and tribological properties of carbon black reinforced nitrile butadiene rubber after water swelling: experiments and molecular dynamics simulations. Tribol Int 217:111685.
30. Song Z, Li Y, Yang B (2021) The interfacial load-transfer enhancement mechanism of amino-functionalised carbon nanotube reinforced epoxy matrix composites: a molecular dynamics study. Compos Sci Technol 209:108790.
31. Wang T, Yang B, Wang S, et al (2026) Comparative study of mechanical and tribological properties of different fiber-reinforced NBR composites: experiments and molecular dynamics simulation. Polym Compos pc.71116.
32. Lou W, Xie C, Guan X (2023) Molecular dynamic study of radiation-moisture aging effects on the interface properties of nano-silica/silicone rubber composites. npj Mater Degrad 7:32–44.
33. Wang X, Huang C, Wang X, et al (2024) Multiscale simulation study on radiation aging of EPDM and preparation of radiation-resistant materials. Compos Sci Technol 252:110595.
34. Jiang S, Li Y, Yong Z (2024) Compatibility analysis between NATURAL RUBBER/POLYBUTADIENE RUBBER and protective waxes based on experiments and materials studio simulations. J Appl Polym Sci 141:e55468.
35. Chen Z, Xing Y, Cao J, et al (2023) Leakage analysis of PEMFC sealing system considering temperature cycling. Energies 16:5475.
36. Quezada GR, Toro N, Saavedra J, et al (2021) Molecular dynamics study of the conformation, ion adsorption, diffusion, and water structure of soluble polymers in saline solutions. Polymers 13:3550.
37. Barney CW, Helgeson ME, Valentine MT (2022) Network structure influences bulk modulus of nearly incompressible filled silicone elastomers. Extreme Mech Lett 52:101616.
38. Hayashi Y, Shiomi J, Morikawa J, Yoshida R (2022) RadonPy: automated physical property calculation using all-atom classical molecular dynamics simulations for polymer informatics. npj Comput Mater 8:222.
39. Choi W-J, Lim J, Kang I, et al (2025) Enhanced performance and durability of sealing gasket for polymer electrolyte membrane fuel cells and water electrolyzer by C–C coupling of functionalized 2D boron nitride nanoflakes. Adv Compos Hybrid Mater 8:382.
40. Yoo J, Lee YH, Park J, et al (2024) Study on low temperature and durability characteristics of gasket for polymer electrolyte membrane fuel cell (PEMFC) depending on cross-sectional geometry. Int J Hydrogen Energy 50:1194–1206.
41. Yao H, Yang D, Lu Y, et al (2024) Screening of sealing materials for PEM fuel cell applications based on weight factor method. J Appl Polym Sci 141:e54833.
42. Qiu D, Liang P, Zhao X, et al (2022) An analytical model for gas leakage through contact interface in proton exchange membrane fuel cells. Int J Hydrogen Energy 47:32273–32286.
43. Xu R, Gil L, Singer J, et al (2026) Leakage at interfaces: a comprehensive study based on persson contact mechanics theory. Tribol Int 214:111352.
44. Huang X, Liu S, Yu X, et al (2022) A mechanism leakage model of metal-bipolar-plate PEMFC seal structures with stress relaxation effects. Int J Hydrogen Energy 47:2594–2607.