Molecular Dynamics Simulation of The Influence of the *Trans*-structure in the Molecular Chain Structure of Natural Rubber On Its Tensile Stress

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Abstract

Predicting the influence of *trans*-structures in the molecular chain structure of natural rubber (NR) on its tensile stress using molecular dynamics (MD) simulations. In this study, establish two all-atom models, all *cis*-structure model (model-1), containing 2% *trans*-structure and 98% *cis*-structure model (model-2), and calculated the cohesive energy density (CED) of the model to determine the feasibility of the model to simulate NR. Then, uniaxial tensile simulations were carried out for both models and it was found that the presence of the inverse structure reduced the tensile stresses in the models. This study is an important theoretical guide to the preparation of high-performance isoprene rubber (IR).

1. Introduction

Natural rubber (NR) is used in a wide range of industrial applications such as automotive tires, drive belts, and packaging due to its unique molecular composition and structure [1–4]. NR has a highly *cis*-structure with a small amount of *trans*-structure in the molecular chain structure. Tanaka in 1989 used ^{13}C-NMR to determine the molecular chain structure of NR, which consists of thousands of *cis*-1,4-isoprene units, 2 to 3 *trans*-1,4-isoprene units, and dimethylallyl linkages [5]. NR contains a large amount of *cis*-1,4-polyisoprene and about 2% *trans*-structure [6].

MD simulation is a technique for modeling the properties of materials at the molecular scale. Simulation methods are used to elucidate the laws governing the motion of particles in time and space due to interacting forces in a system. As a first step, we must create models of the forces and laws of motion of the particles in the system, relating the microscopic inter-particle forces to the theory of Newtonian mechanics, determining the form of the inter-particle interactions and the laws governing the motion of the particles; we can then use computers to calculate the trajectories of collections of particles to determine their static and dynamic properties [7–10].

In 1956, Wainwright and Alder used MD to study the equation of the state of gaseous and liquid substances using the molecular hard balloon model. The results of the study showed that multidimensionality can guide practice theoretically and play an important role in solving many practical problems [11]. The first MD simulation of a real material model to predict the radiation hazards of diamond crystals was performed in 1959 by a group led by Vineyard in Brookhaven [12]. Rahman conducted the first MD simulation of a real fluid (hydrogen) using the continuous potential model in 1963 [13]. The time and space scales of early simulations were severely limited due to the computer's slow speed and inadequate memory.

Nowadays, computer technology is rapidly evolving, and the processing speed and storage space of computers are increasing, allowing people to solve complex material analysis problems using complex models [14–15]. People currently use the finite element simulation analysis method and the molecular simulation method as simple, reliable, and accurate computer simulation methods [16–18]. MD simulation methods have increasingly been implemented in the field of polymer materials since the

beginning of the twenty-first century [19–21]. It is difficult to explain in detail due to the complex structure of polymer materials and the large molecular chain framework. To save calculation time, coarse-grained and all-atom models are commonly used to simulate polymer materials, and the Monte Carlo (MC) method is often used to create material models [22–23]. In addition to traditional experimental methods, MD simulation is an effective theoretical tool for studying the relationship between material structure and performance. It can not only explain experimental results, but it can also predict the effect of structure on material properties to some degree [24].

With the rapid advancement of computer science in recent years, MD simulation technology has grown in popularity in scientific research and practical applications. Researchers can quantify certain parameters that are difficult to obtain in experiments using MD simulations. Researchers can quantify certain parameters that are difficult to obtain in experiments using molecular simulations [25–26]. For example, the fraction of free volume (FFV), solubility parameter (δ), and mean square displacement (MSD) for materials, were conveniently calculated by MD [27–29].

Using the methods of MD simulation, this research aims to predict the influence of the *trans*-structure in the NR molecular chain structure on the tensile stress of NR. In a uniaxial tensile simulation by building model-1 and model-2, the effect of *trans*-structure on the tensile stress of NR was analyzed based on MD simulation results. Provides theoretical guidance for the preparation of high-performance IR.

2. Model And Simulation Details

All theoretical calculations for the quantum mechanics simulations were done in Materials Studio's $DMol^3$ module. Many essential parameters, like entropy (S), enthalpy (H), free energy (G), and so on, maybe determined using the QM simulation. The simulation of QM is based on density functional theory with dispersion correction (DFT), the fundamental properties of multi-particle systems are obtained by solving the Kohn-Sham (KS) equation [30, 31]. The exchange-related potentials in the KS equation were processed using a generalized gradient approximation (GGA) mode in the form of the Perdew-Burke-Ernzerhof (PBE) function [32]. At the same time, three-numerical atomic orbitals enhanced by additional polarisation functions (TNPs) 32 are used as basis sets. Frequency calculations followed the same level as above to confirm that each optimized structure has the minimum energy at all practical frequencies [33].

The Forcite module of the Materials Studio suite was utilized for the molecular dynamics (MD) simulations. Force fields in the condensed phase of condensed Phase optimized molecular potential field (COM-PASS) for atomic simulation studies were chosen. It can simulate not only the thermodynamic properties of isolated molecules but also the exact condensed structure and vibrational frequencies [34]. It is widely used for pre-structural, thermophysical, and conformational properties. The Andersen technique is used to regulate temperature, and non-bonding and van der Waals interactions are calculated using conventional atom-based modeling methods [35]. The construction procedure of the amorphous cells is shown in Figs. 1 and 2.

To verify the feasibility of the model to simulate NR, we introduce the solubility parameter (δ), δ describes the cohesion between molecules and is important for assessing the compatibility of different materials. δ is specified as the square root of the cohesion energy density (*CED*) [36]. Where *CED* stands for cohesion energy density, E_{coh} is the change in internal energy of vaporization, V is the molar volume, ΔH_{vap} is the enthalpy of vaporization, *R* is the gas constant and T is the absolute temperature. The solubility parameters of model-1 and model-2 are shown in Table 1. The simulated values of δ are within the range of the experimental values, and the model of the real material can be replicated by such models.

$$\delta = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} = \sqrt{\frac{\Delta H_{vap} - RT}{V}} \quad (1)$$

Table1 Parameters of physical properties for NR at 298 K and 1 atm

	CED (J/cm^3)	δ [(J/cm^3)]$^{0.5}$
Model-1	282.2	16.8
Model-2	265.7	16.3
Experiment	280.0	16.2-17.0

3. Results And Discussion

To obtain the mechanical properties of the NR model, axial stretching operations were performed using longitudinal simulations. During the longitudinal simulation, the stretching process is simulated by varying the shape of the simulation box uniformly in the x-direction. During the stretching process, a pressure of 1 atmosphere is applied in the y and z directions. The tensile stress in the x-direction in the simulation box can be calculated using the Vera stress method [37]. A diagrammatic representation of the tensile simulation is shown in Fig. 3.

$L(t) = L_0(1 + \text{erate} \times dt)$ (2)

Where L_0 and L(t) are the initial and final lengths of the model in the stretching direction, respectively, and it is the elapsed time. In all simulations in this study, the stretching rate was set to 5 × 10-8 fs^{-1}. The stress-strain curves of model-1 and model-2 were obtained using the tensile simulation results (Fig. 4). The results show that *trans*-structure reduces the stresses in the model. This means that the presence of *trans*- structures should be avoided in the preparation of isoprene rubber to improve the tensile strength of IR. The regularity of the molecular chain structure has a strong influence on the strength of the raw rubber. As the *cis*-1,4-polyisoprene content decreased, the strength of the raw NR decreased significantly, which is thought to be related to the decrease in crystallinity [38].

In statistics, MSD is a physical quantity used to describe the deviation of a particle between its position and its relative position over time. MSD can be used to describe the mobility of polymer chains [39]. The expression of MSD is as follows [40]:

$$MSD = \frac{1}{N}\sum_{t=0}^{N}(x_t - x_0)^2 \quad (3)$$

In the formula, N is the total number of molecular chain conformations involved in the statistics in the NPT ensemble dynamics result from the trajectory file, x_t is the vector of the molecular chain centroid at the moment, and x_0 is the vector of the molecular chain centroid at the initial moment. MSD is also measured using the Analysis option under the Forcite module. Select Mean square displacement in Forcite Analysis to determine the set of all molecular chains defined when calculating the mean square radius of gyration, as well as the second half of the MPT ensemble dynamics procedure trajectory (That is the trajectory from 130ps to 240ps because the second half of the trajectory is the model close to balance) for calculation and analysis.

Fig. 5 is the MSD diagram of two models obtained by MD simulation at 298 K and vulcanization temperature (423 K). The relative mobility of the two models is model-1 > model-2 at 298 K and 423 K. Combined with the stress-strain curves of model-1 and model-2, it can be seen that there is a correlation between the tensile strength of NR and its mobility.

4. Conclusions

In this study, MD simulations were used to predict the influence of the *trans*- structure in the molecular chain structure of NR on its tensile stress. It was found that a 2% *trans*-structure decreased the tensile stress of NR. This means that the *trans*-structure disrupts the regularity of the molecular chain structure of NR and the crystallinity of NR is reduced. There is a correlation between the tensile strength of NR and its mobility. Furthermore, MD simulations provide a quantifiable theoretical guide to understanding the structure-property correlation of materials, which is very useful for material design.

Declarations

Author contribution All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Zechun Li. Research design, the acquisition, analysis, and interpretation of data by Changjin Yang, Approval of the submitted and final version were performed by Fuchun Zhao. Research design, the acquisition, analysis, and interpretation of data by Yanchan Wei. Approval of the submitted and final version was performed by Shuangquan Liao. The first draft of the manuscript was written by Zechun Li and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability All the analyzed and generated data used for this study are available along with this manuscript.

Code availability Code availability N/A.

Competing interests The authors declare no competing interests.

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Figures

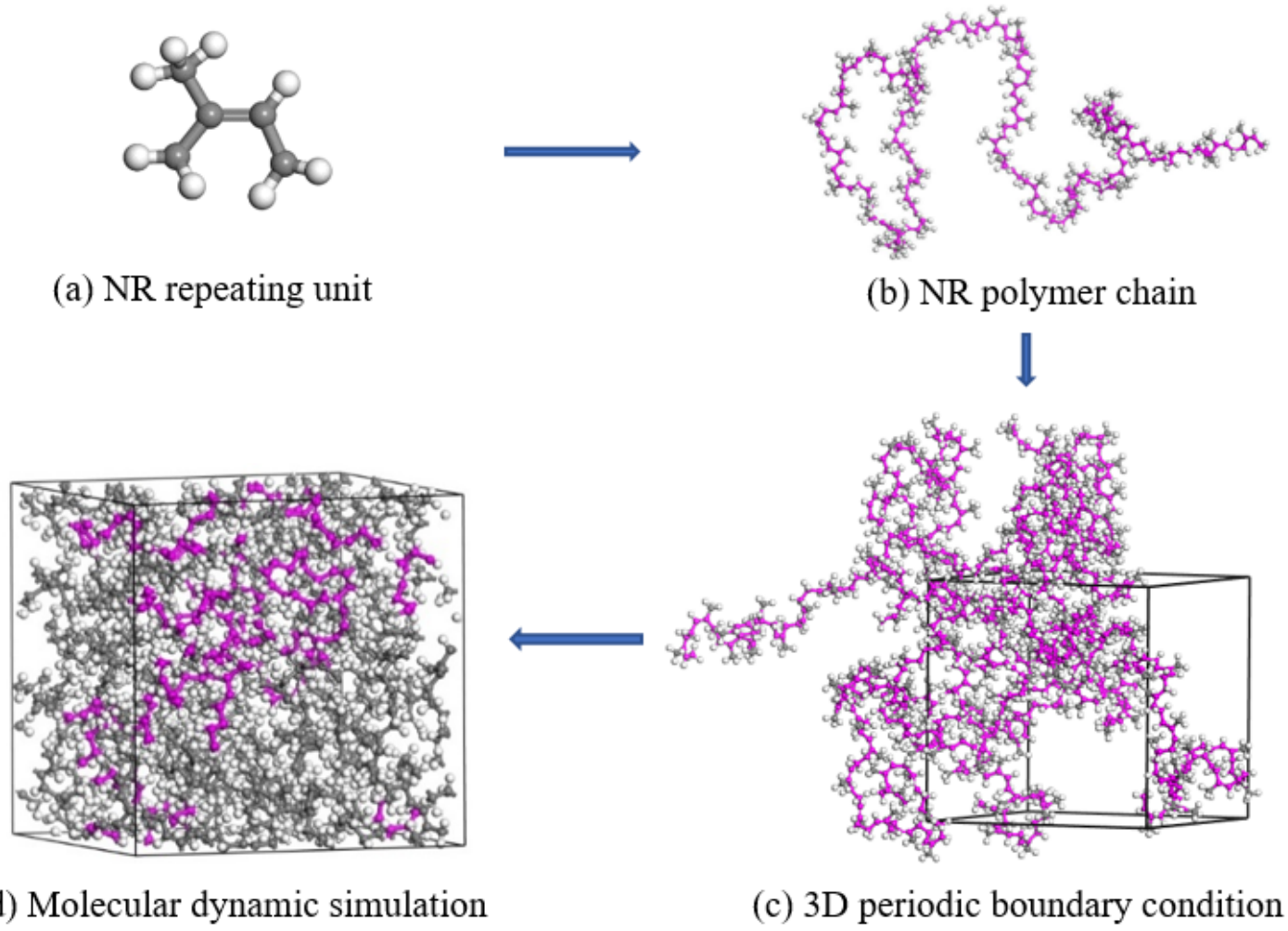

Figure 1

Construction process of NR amorphous cell model-1. (The white and gray spheres represent hydrogen and carbon atoms, respectively. In addition, the magenta spheres in the NR repeating unit and chain also represent C atoms.)

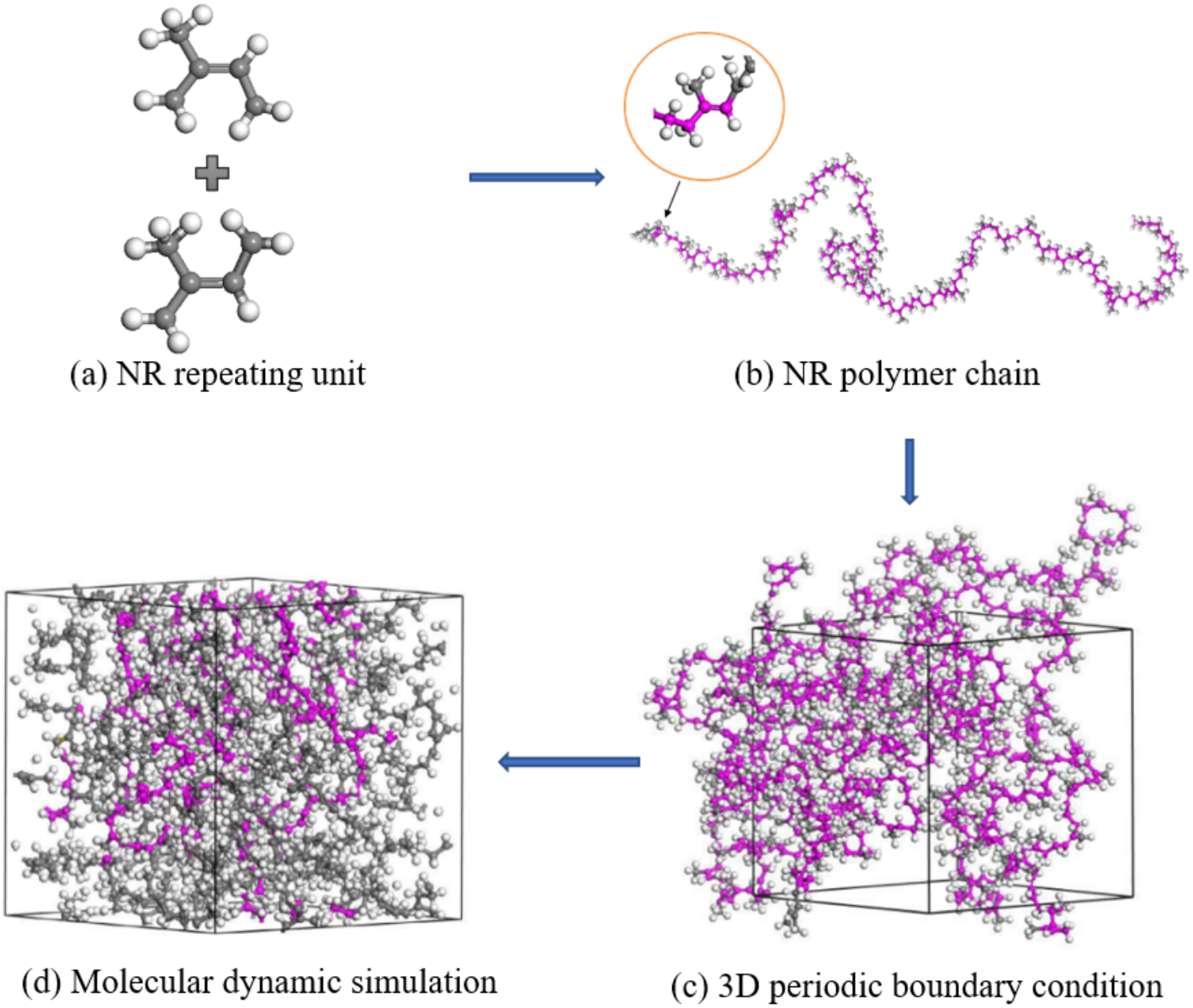

Figure 2

Construction process of NR amorphous cell model-2. (The white and gray spheres represent hydrogen and carbon atoms, respectively. In addition, the magenta spheres in the NR repeating unit and chain also represent C atoms.)

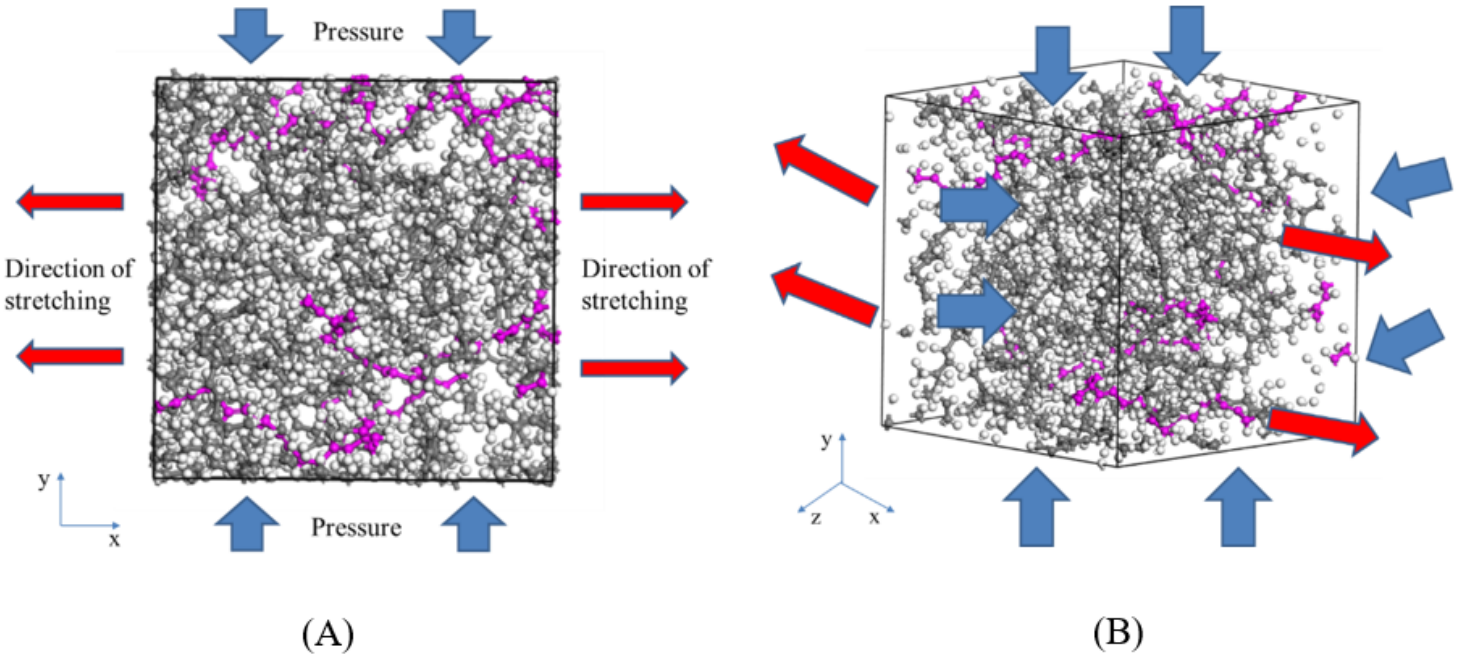

Figure 3

Schematic of the tension in the MD simulation

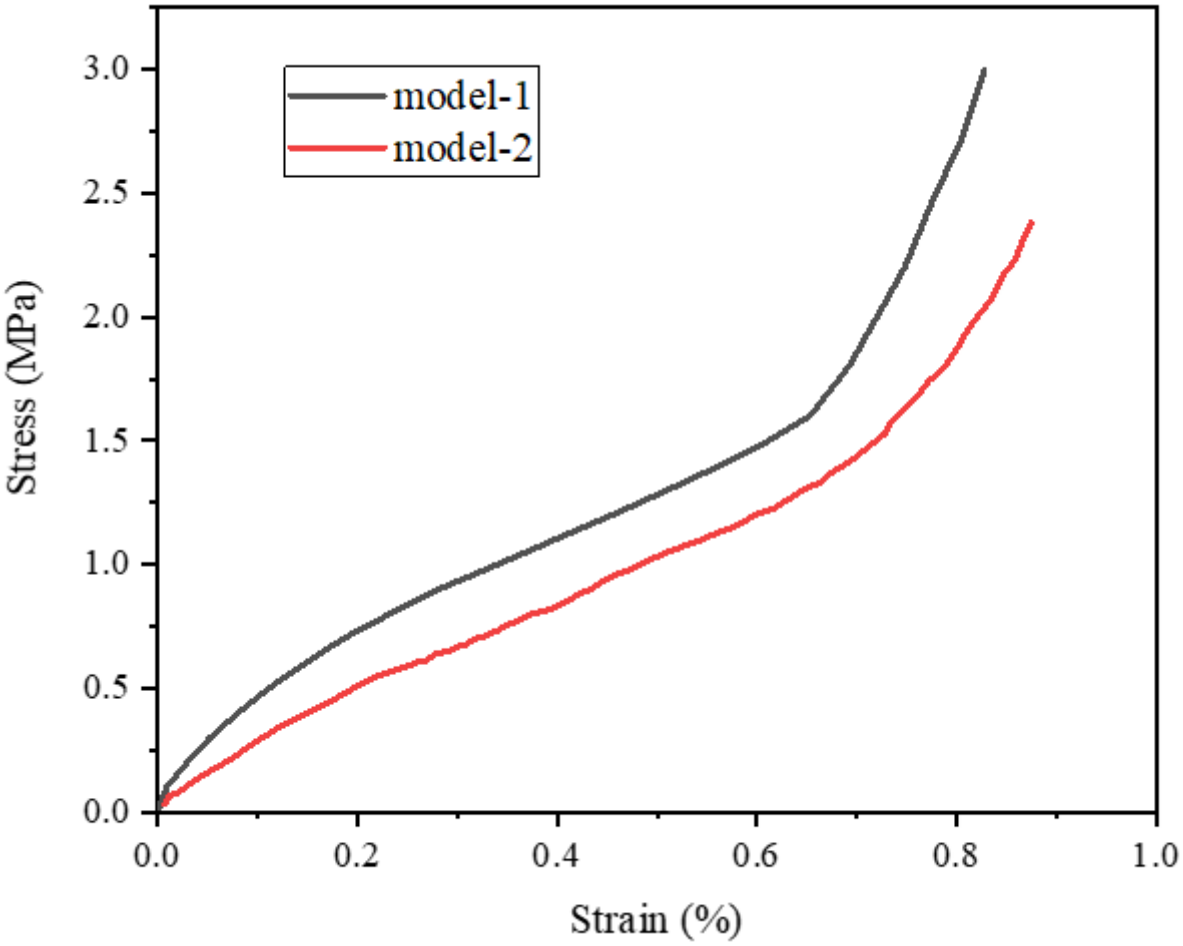

Figure 4

Stress-strain curves of model-1 and model-2

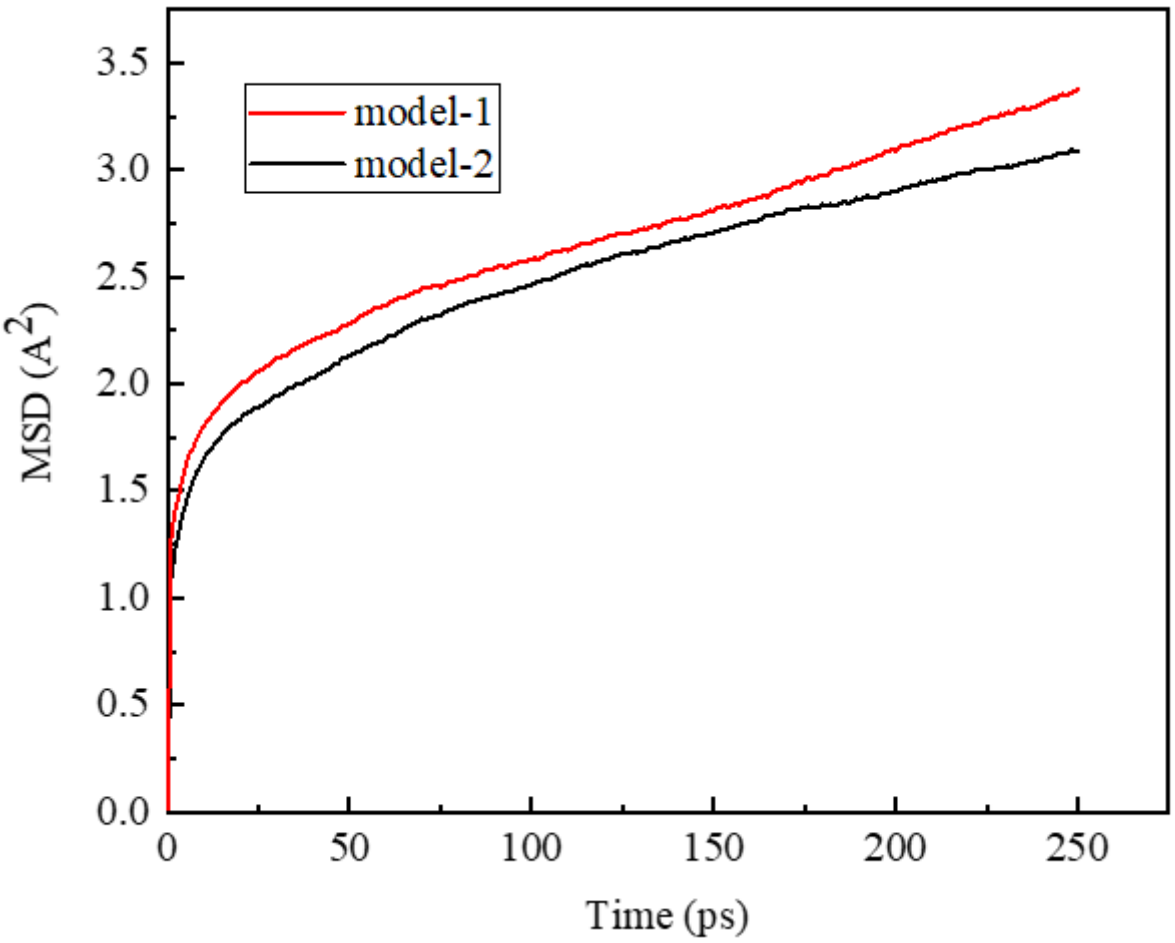

Figure 5

MSD curves of model-1 and model-2 during MD simulations.