Supporting Information

All-atom molecular dynamics simulation of structure, dynamics and mechanics of elastomeric polymer materials in wide range of pressure and temperature

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CONTENTS

Section 1. Models of rubber simulation systems

The optimized structures of the repeating units for the rubber types are depicted in Fig. S1 (a-e). The rubber molecular chains were constructed using the Build Polymers module, where BR and NR represented the construction of homopolymer molecular chains and SBR represented the construction of random copolymer molecular chains. After optimization, the structures of the three rubber molecular chains were obtained, as illustrated in Fig. S2.

For the spherical SiO_2 nanoparticle model, the α-quartz unit cell structure available in the MS software database was selected. Silicon and oxygen atoms located beyond a distance of 5 Å from the nanoparticle center were removed from this structure, resulting in a cluster consisting of 16 Si atoms and 27 O atoms. After neutralization, the SiO_2 nanoparticle underwent optimization using the same method as mentioned.[1] The resulting structure of the spherical SiO_2 nanoparticle is presented in Fig. S1 (f).

Subsequently, the rubber molecular chains were assembled using the Amorphous Cell module at a lower density, completing the construction of the amorphous pure rubber simulation system and rubber/SiO_2 nanocomposite simulation system. Geometric optimization and energy minimization were performed on the rubber simulation systems to eliminate chain overlaps and other inconsistencies. The resulting models of the pure rubber and rubber/SiO_2 nanocomposite systems are depicted in Fig. S3.

In this study, the COMPASS (Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies) force field was employed to describe the molecular interactions within and between components of the rubber simulation system. The

COMPASS forcefield, initially developed by MSI Corporation in 1998, is a meticulously optimized first-principles approach that encompasses a wide range of elements from the periodic table, accounting for their diverse valence states. It has demonstrated remarkable capabilities in accurately predicting the properties of prevalent inorganic molecules, organic molecules and polymers across an extensive range of temperature and pressure. Consequently, the COMPASS forcefield is regarded as a highly sophisticated and comprehensive full atomic-type force field, enabling reliable simulations of the rubber system in this research.[2, 3]

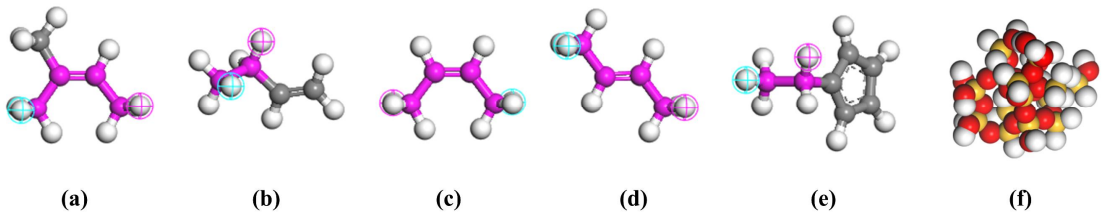

Fig. S1 Repeat units of rubber: (a) cis-1,4-isoprene unit, (b) 1,2-butadiene unit, (c) cis-1,4-butadiene unit, (d) trans-1,4-butadiene unit, (e) styrene unit and (f) spherical SiO_2 nanoparticle with a saturated surface. The white, gray, purple and red beads represent the hydrogen, carbon, carbon and silicon atoms.

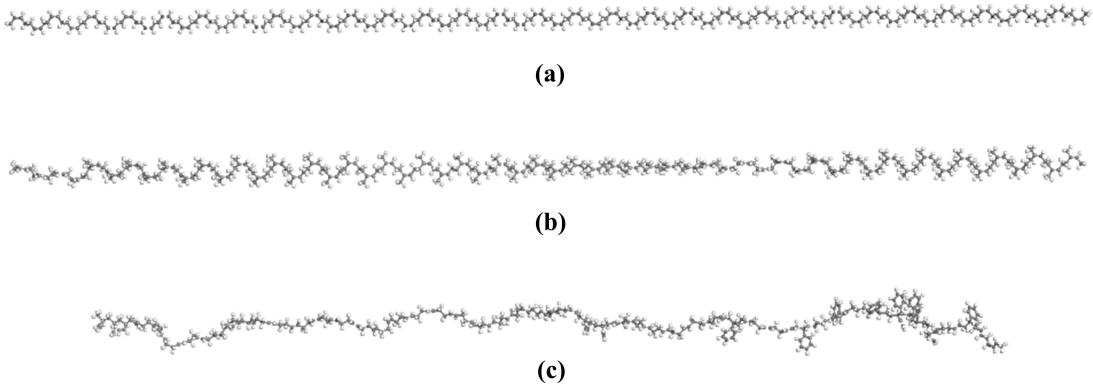

Fig. S2 Molecular chains of rubber: (a) BR, (b) NR and (c) SBR

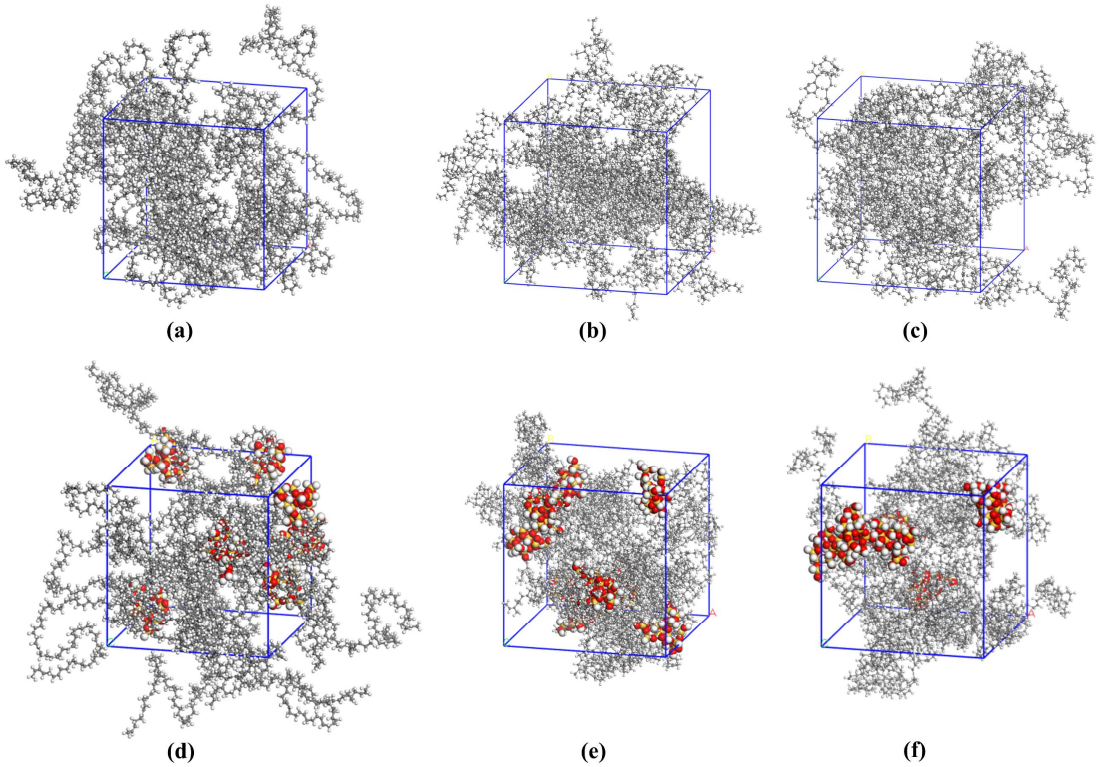

Fig. S3 Simulation systems of pure rubber: (a) BR, (b) NR and (c) SBR, rubber/SiO_2 nanocomposites: (d) BR, (e) NR and (f) SBR. The white, gray and red beads represent the hydrogen, carbon and silicon atoms.

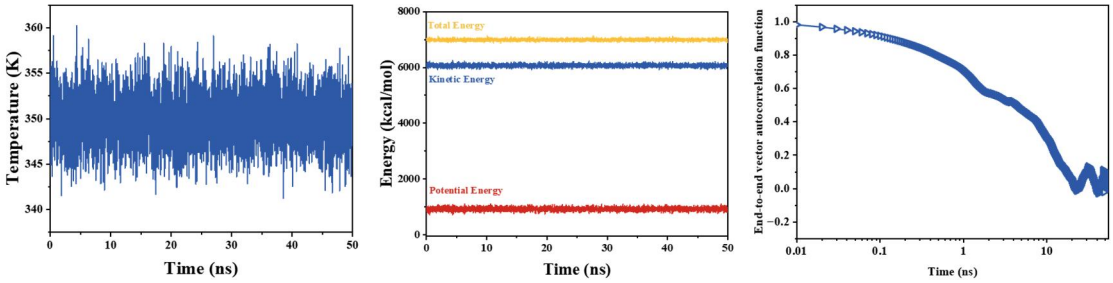

Fig. S4 Dynamic (a) temperature-time (b) energy-time and (c) end-to-end vector correlation function curves of the molecular dynamics simulation

Section 2. Stress-strain behavior of pure rubber

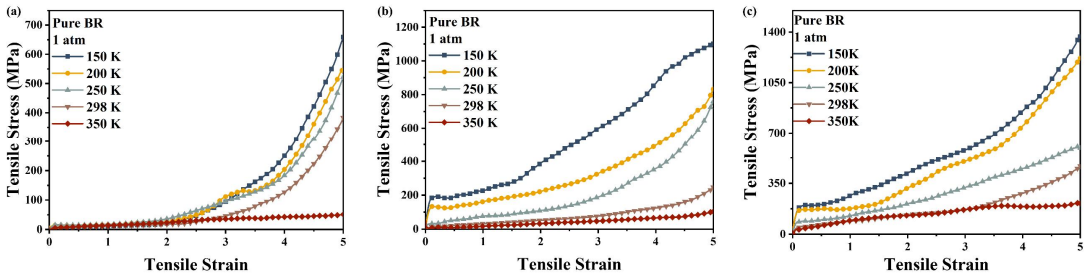

Fig. S5 Stress-strain behavior of pure BR at 1 atm and different temperature under tensile rate of (a) 10^8/s, (b) 10^9/s and (c) 10^{10}/s.

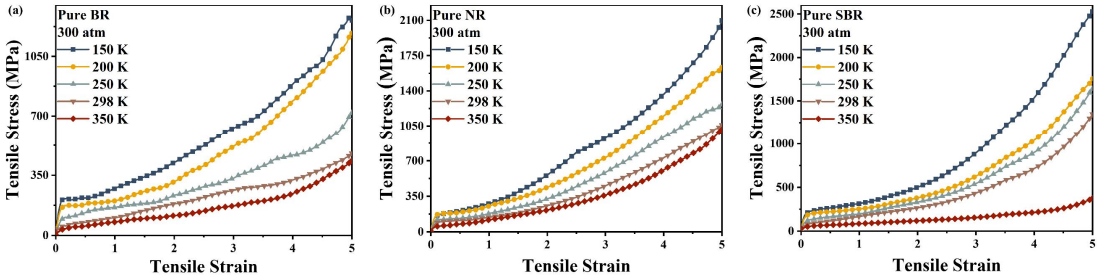

Fig. S6 Stress-strain behavior of pure rubber at 300 atm and different temperature: (a) BR, (b) NR and (c) SBR.

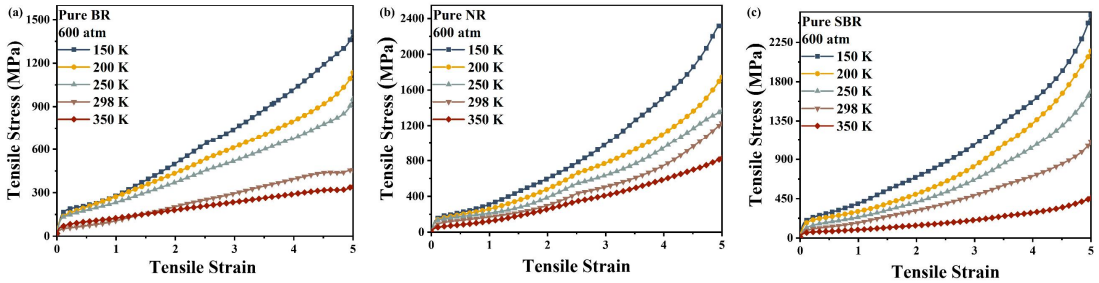

Fig. S7 Stress-strain behavior of pure rubber at 600 atm and different temperature: (a) BR, (b) NR and (c) SBR.

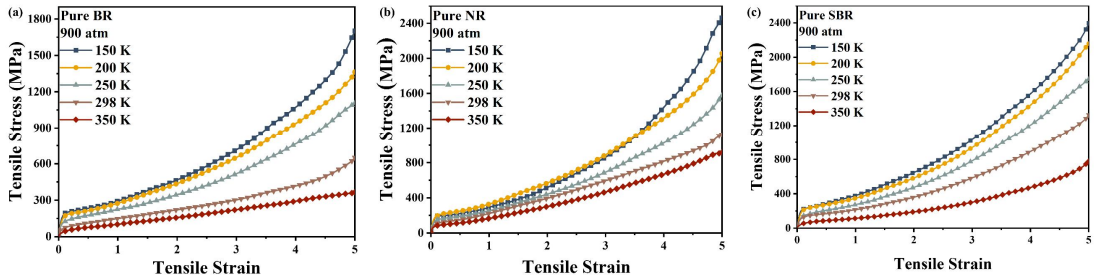

Fig. S8 Stress-strain behavior of pure rubber at 900 atm and different temperature: (a) BR, (b) NR and (c) SBR.

Section 3. *P-V-T* relationship and bulk modulus of rubber/SiO_2 nanocomposites

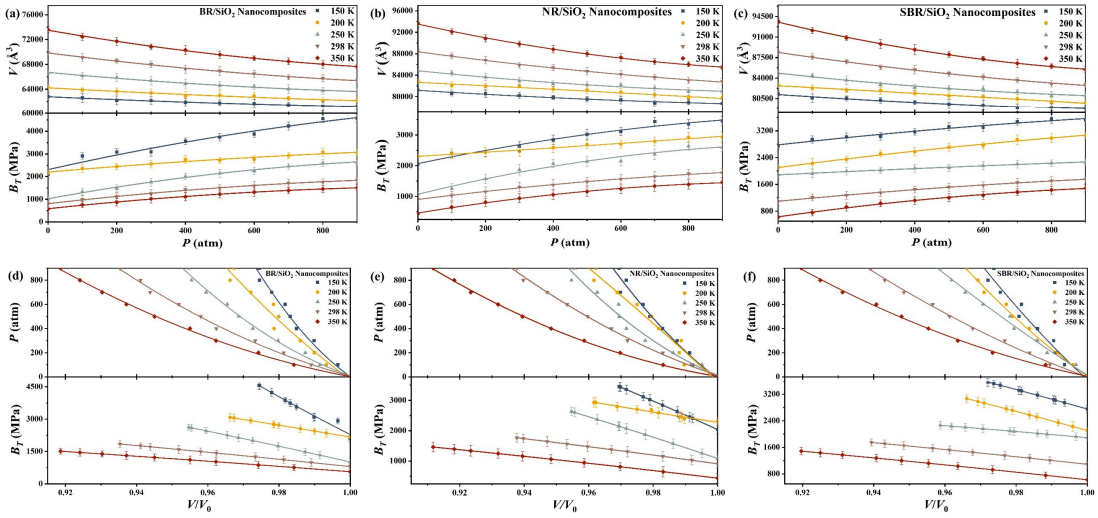

Fig. S9 Pressure-dependent volumes and isothermal bulk modulus of rubber/SiO_2 nanocomposites at different temperature: (a) BR, (b) NR and (c) SBR. Pressure and isothermal bulk modulus of rubber/SiO_2 nanocomposites versus volume ratio at different temperature: (d) BR, (e) NR and (f) SBR. where V_0 refers to the volume at zero pressure.

Section 4. *P-V-T* relationship and bulk modulus of crosslinked rubber

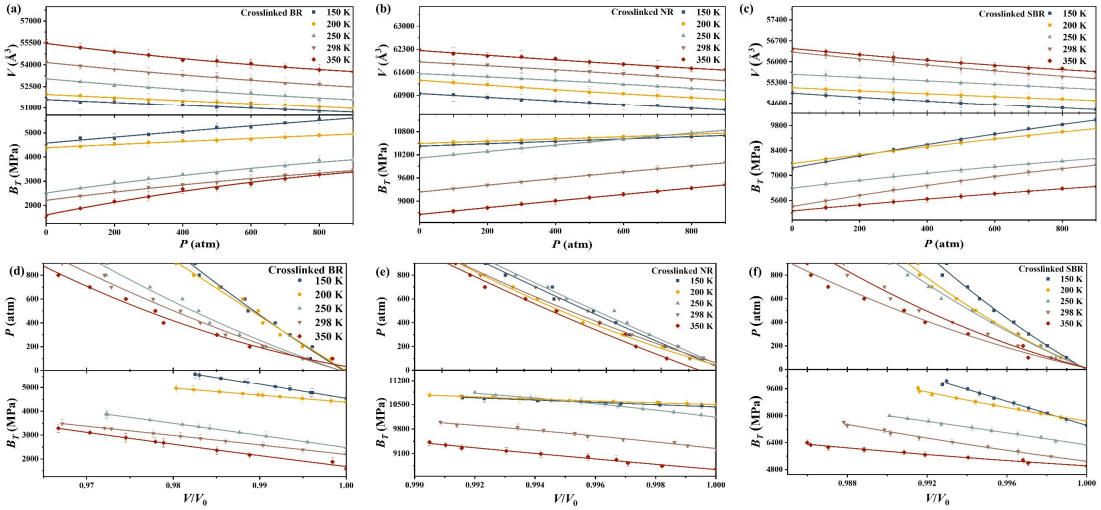

Fig. S10 Pressure and isothermal bulk modulus of crosslinked rubber versus volume ratio at different temperature: (a) BR, (b) NR and (c) SBR. Pressure-dependent volumes and isothermal bulk modulus of crosslinked rubber at different temperature: (d) BR, (e) NR and (f) SBR.

REFERENCES

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