



Research paper

Fully atomistic molecular dynamics simulation of nanosilica-filled crosslinked polybutadiene

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ABSTRACT

We report on the first fully atomistic simulation of sulfur-crosslinked *cis*-1,4-polybutadiene (PB) rubbers, both unfilled and nanosilica-filled. A well-integrated network is built by crosslinking the coarse-grained precursor PB chains. The initial configurations for subsequent molecular dynamics simulations are obtained by reverse mapping of well-equilibrated coarse-grained systems. Thermal and mechanical properties of the PB-based elastomers are predicted in reasonable agreement with experiment. The inclusion of silica nanoparticles into the model rubber increases the glass transition temperature and elastic modulus. Under tensile loading conditions, the formation of structural defects (microcavities) within the polymer bulk is observed for nanocomposite at the elastomer/nanoparticle interfaces.

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1. Introduction

Crosslinked elastomeric materials, both unfilled and filled, have numerous applications ranging from automotive sector to biomedical devices [1,2]. These materials can also be used for producing innovative classes of devices such as nanocomposite-based stretchable strain sensors, solar cells, and e-papers. During both their processing and application, these materials can experience large mechanical stresses and thermal gradients. However, considerable information about the mechanical and thermal responses of crosslinked elastomers remains to be uncovered. Even though the use of different nanofillers is ubiquitous for the last decade, satisfactory understanding and modeling of the micromechanisms by which nanofillers alter the mechanical and thermal behaviors of elastomeric materials has still not been completely realized.

Elastomer nanocomposites, in which particles of nanoscale dimension are dispersed in a crosslinked polymer matrix, have been the subject of extensive research in recent years using experimental, theoretical and simulation methods. In order to elucidate the structure–property relationships of these materials and provide the direct quantitative comparison between experiment and theory, molecular level modeling and simulation is required. However, due to high complexity of nanofilled elastomers, highly

idealized coarse-grained (CG) models, such as united atom models and bead-spring models, are mainly employed for simulating nano-filled elastomers. There are nice reviews partly covering this subject [3–8].

Despite the large number of publications on CG modeling of rubbers, to our knowledge, no systematic simulation research exists addressing the effect of nanoparticles (NPs) on the thermo-mechanical properties of crosslinked elastomers modeled at the all-atom level. This is one of the reasons why the microscopic mechanism of polymer reinforcement remains a matter of debate [9,10]. In particular, one major open question is how stresses and strains are transmitted in nanofilled elastomers. Besides, because of the uncontrolled manner in which elastomeric networks are generally prepared, there is little reliable quantitative data on the structure–properties relationship for these materials.

In this Communication, our objective is to simulate the structural and mechanical properties of sulfur-crosslinked *cis*-1,4-polybutadiene (*cis*-1,4-PB), which is one of the main components of synthetic butadiene rubbers (BRs). In particular, we are interested in the structural rearrangements of the nanocomposite subjected to tensile deformation under high strain-rate loading conditions. Very recently, interest in this traditional polymer material has increased drastically due to the possibility to prepare the thermally reversible crosslinked PB elastomer using Diels–Alder reaction [11]. In this way, vitrimer-like (covalent adaptable) PB

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networks could be thermally recycled like plastic materials to prolong its service life and solve its unrecyclable problem.

It should be noted that uncrosslinked polybutadiene has been extensively simulated in recent years. Atomistic simulations of two isomers of polybutadiene, *cis*-1,4-PB and 1,2-PB, have been conducted by Theodorou and co-workers using the end-bridging Monte Carlo algorithm and the method of molecular dynamics [12,13]. Narros et al. have investigated the short-range order in 1,4-PB by combining fully atomistic MD and neutron diffraction [14]. In a series of recent publications, Maurel et al. have developed a mesoscale model to study static and dynamic properties of PB melt [15–17]. Also, these authors have investigated the interaction between *cis*-1,4-PB chains and a silica surface [17]. Atomic MD simulation has been employed to calculate the glass transition temperature of *cis*- and *trans*-1,4-PB [18]. Solar and Paul have presented results from MD simulations of a chemically realistic model of 1,4-PB chains confined by crystalline graphite walls [19]. We stress that all these studies focus on linear macromolecules. Therefore, the results reported in the present work can be considered as an extension of these simulations to crosslinked PB systems and PB-based nanocomposites.

2. Model and simulation technique

A linear *cis*-1,4-polybutadiene (PB) was used as a model polymer for crosslinking by sulfur. Both unfilled and silica nanofilled PB networks were simulated using a multiscale modeling approach described in detail previously [20]. This approach includes the following stages: (i) atomistic structures are first coarse grained into beads and springs, and their atomic potentials are replaced by effective site-site potentials between beads; (ii) using dissipative particle dynamics (DPD), the CG monomers are crosslinked to form polymer network; (iii) a reverse mapping procedure is then applied to recover and refine the atomistic structure of the system; (iv) after equilibration, fully atomistic MD is performed to predict properties of the crosslinked materials.

Rubbery networks were prepared in this study by random crosslinking of the precursor 80-unit PB chains. Short sulfur chains S_3 were taken as a curing agent. The ratio between sulfur and polymer species was close to 1.6. This ratio provided the crosslink density comparable to that observed experimentally [1]. With the sulfur/polymer composition and polymer length used here, the average network strand length is expected to be about 40–50 for a fully crosslinked network. Nearly spherical silica nanoparticles (SNPs) of diameter ≈ 25 Å were simulated. They were built from the crystal structure of β -cristobalite. All surface silicon atoms were bonded to three surface oxygen atoms which were saturated with hydrogen atoms to satisfy their chemical valence [21]. Thus, the NP surface was modified with polar hydroxyl groups. Then we performed geometry optimization on the SNPs with the class II polymer consistent force field (PCFF) [22] supplemented by the parameters developed and tested for layered silicates [23]. The number density of silanol groups on the surface of the relaxed nanoparticle is 0.064 per Å², which is close to the high end of the experimental OH surface density range (0.042–0.062 OH per Å² [24,25]). The surface fractions of different types of silanol groups Si(OH)_x are as follows: 0.45, 0.49 and 0.06 for $x = 1, 2$ and 3, respectively. Note that the presence of single, double and triple (relatively rare) silanol groups was confirmed by the IR spectroscopy of silica surfaces [26] and the first-principles molecular dynamics simulations [27]. It should also be kept in mind that the structure of silica surface strongly depends on thermal treatment.

One of the most important ingredients of our multiscale simulation strategy is the construction of a coarse-grained (CG) system. To do this adequately, we have developed an automatic approach

based on the method of neural-gas (NG) networks, the so-called topology-generating network [20]. In the present study we used this technique with a coarse-graining parameter, which defines spatial resolution (coarse-graining level), equal to 1.

In our mesoscale simulations, we represented the CG species by the bead-spring model, which is the standard model in DPD simulations [28]. Adjacent beads interact via a quasi-harmonic bond force of the form $f_b = k_b[A_b(1 + \Delta_b^2(1 + \Delta_b^2))]b_0/r$, where $A_b = r/b_0 - 1$ and b_0 is the equilibrium bond length that coincides with the characteristic bead size σ , while a simple harmonic bending potential $k_b(\theta - \theta_0)^2$ is applied to three neighboring connected beads. The force parameters k_b and k_θ define the stretching and bending stiffness and are fixed at $100 k_B T/\sigma^2$ and $100 k_B T/\theta_0^2$, respectively. The Flory–Huggins (FH) binary interaction parameters $\chi_{\alpha\beta}$ and the corresponding DPD short-range repulsive interaction parameters $a_{\alpha\beta}$ of species α and β are directly related to the Hildebrand single-component solubility parameters δ_α and δ_β . From the intrinsic viscosities of PB samples in cyclohexane–toluene mixtures, He et al. [29] obtained $\delta_{PB} = 16.8\text{--}18.2 \text{ MPa}^{1/2}$. For sulfur, an experimental literature value gives $\delta_S = 26 \text{ MPa}^{1/2}$ [30]. These values of δ together with the reference bead volume V_b of the beads were used to estimate FH cross-interaction parameters from the relationship $\chi_{\alpha\beta} = (V_b/k_B T)(\delta_\alpha - \delta_\beta)^2$, while $\chi_{\alpha\alpha} = 0$ by definition. The energy parameters relating to the SNP–polymer interaction can easily be evaluated from the cohesive energy but, for simplicity, we set $\chi_{SNP, PB} = \chi_{SNP, S} = 0$. Specific values of these parameters are not essential; it is only important to keep the SNPs impenetrable. To simulate the network formation process, we used a model of chemical reaction systems based on the well-documented DPD framework [28] and our concept of composite DPD particles which are composed of two different types of CG sites: non-reactive beads and reactive linkers (for more detail, see Ref. [20]).

The reactive CG species were placed randomly into the periodic simulation box containing 64 identical SNPs. To avoid the aggregation of nanoparticles, they were initially placed on simple cubic lattice sites (a $4 \times 4 \times 4$ grid) and their positions were not updated during the relaxation and crosslinking phase. Therefore, we modeled a nanocomposite material with uniformly dispersed nanoparticles. The number fraction of NPs was fixed at 0.062 (this value corresponds to 14.4 wt%).

After a long equilibration of the precursor melts, the chemical crosslinking reactions were simulated. At regular time intervals of 10^3 DPD time steps, randomly chosen pairs of reactive sites belonging to sulfur and polymer unsaturated carbons could form irreversible bonds with a probability of 3×10^{-3} when they are within the reaction distance R_c . The DPD simulations were carried out at constant pressure and constant temperature. The temperature was maintained by the standard DPD thermostat [28] while constant external pressure P_0 was maintained on the faces of the simulation box, allowing the system volume to adjust to the curing. To this end, we used the modified Langevin piston algorithm [31,32] with an applied external pressure of $P_0 = 24 \text{ } \epsilon/\sigma^3$, where σ is the bead size and ϵ is the characteristic energy that measures repulsive interaction between beads and can also be linked to the χ -parameters in a Flory–Huggins-type model. The use of a constant pressure (isobaric) constraint with anisotropic coupling allowed box dimensions to change independently, thereby minimizing the effect of the box size and shape on the final network structure and internal stress.

Because the positions of the CG sites are explicitly associated with the corresponding atom positions, the reverse mapping is straightforward. The reconstructed all-atomistic models of the crosslinked *cis*-PB with/without embedded SNPs comprised about 630,000 and 590,000 atoms, respectively. They were enclosed in the periodic rectangular boxes with an edge length of ≈ 200 Å.

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