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Molecular dynamics simulation study of a fracture of filler-filled polymer nanocomposites

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ABSTRACT

We investigated a fracture of polymer nanocomposites filled with spherical nanoparticles (NPs). The dependences of the fracture on the interactions between the NPs and polymers were examined by coarse-grained molecular dynamics simulations in a deformed box with a Poisson ratio of 0.4. In order to observe the creation of nanovoids, the interaction among the polymers was set to be attractive. When the NP-polymer interaction is attractive, nanovoids appear in the bulk of polymers. On the other hand, for repulsive NP-polymer interaction, nanovoids are created at the surface between the polymers and NPs. At the same time, segregation of NPs is observed. We found that these behaviors depend on crosslink densities.

1. Introduction

Reinforcement of soft materials is an important issue for the development of highly functional rubber materials, such as fuel-efficient tires or oil-sealing rubber parts [1–4]. Such reinforcement is attained by filling functionalized nanoparticles (NPs), and this is controlled in the mixing process for the NPs. Mostly effective interaction among functionalized NPs and polymers is non-repulsive in order to avoid segregation of NPs. For industrial applications, it is considered that the improvement of NP's functionality is much important for the dispersion of the NPs [5,6]. Inhomogeneity at NP's surface of attractive interaction leads to interesting morphology formation as an isolated NP cluster [6,7]. Although morphology formation of NPs in rubber materials is a key issue for mechanical properties, which is described by stress strain relation, interactions among NPs and polymer are more fundamental on toughness and/or fracture of those materials. The toughness of rubber materials is sometimes understood by the fractures of those materials, which are classified into cohesive or interfacial fractures [8–10]. For example, in the peeling process of a soft pressure-sensitive adhesive, both fracture modes can be found [11,12]. In the fracture process, nanovoids are first derived, which grow to form a microcavity, and finally the material breaks. Therefore, it can be distinguished that the creation and growth processes of nanovoids are key steps in the study of the fracture mechanism, and nanovoids formed during the fracture processes of rubber materials have been the subject of growing interest in the research area of rubber materials.

A nanovoid is defined as a cavity of nano size, which is smaller than a few tens of nanometers. Due to their size, nanovoids are too difficult to detect. Recently, Creton and co-workers have studied nanovoids in the fracture process of carbon black-filled styrene-butadiene rubber by using small-angle X-ray scattering analysis [13]. If the cavity becomes larger than a few microns, it can be observed by using an optical microscope. Nanovoids of 20–40 nm can be detected in the behaviors of two-dimensional scattering patterns, and measurement of the variation in volume by a digital image correlation method. Although nanovoids can be observed, this is limited to static nanovoids; the structures of voids in dynamic processes have not yet been obtained.

To study the dynamic process of polymeric materials, coarse-

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grained molecular dynamics (cgMD) method is used. This can be applied to several kinds of polymeric materials. Recently, significant progress in simulation techniques has been made in both simulation software and computational tools. Using these tools, we have performed cgMD simulation for thousands of filler-filled polymer nanocomposites (PNCs) in a box corresponding to the sub-micron scale [14]. In the cgMD, detailed movements of polymer chains can be observed. Polymer chain behaviors near the NP-Polymers interface and/or crosslink points are very interesting in the viewpoints of both academia and industries. For the case without nanovoids, distributions of coarse-grained particles and bond orientations near the interface have been examined in the previous work [14]. Moreover, preliminary analysis of local polymer chain dynamics by mean square displacement are performed by the authors. For the case with nanovoids near the interfaces, these analyses can not be directly applied because of absence of polymer chains around NPs. Detailed analyses of polymer behaviors near the interfaces are under consideration. Because the examined system is very complex and complicated, we considered that some probing tests are required to reveal molecular-level mechanism. For example, we have plans to investigate effects of connections between NPs and polymers, size and shape of polymers, and their distribution. Studies in these directions are in progress.

In the present study, we investigated the fracture processes of filler-filled rubbers using cgMD simulations. The present studies focus on difference of behaviors of nanovoids due to NP-polymer interaction, although effect of aggregated structure of NPs is important on its mechanics. Thus, we considered well dispersed initial morphology given by a certain hard sphere configuration as the first investigation of successive studies for filler filled polymer networks. Note that some industrial processes are not equilibrium and NPs are forcedly dispersed by mechanical mixing and crosslinking. Therefore, we considered that simulation studies starting from the random configuration of NPs can be justified. We performed uniaxial elongation of PNCs under an NLpT condition with a Poisson ratio of 0.40 in order to develop fundamental analyses and obtain preliminary results prior to large-scale simulations with a Poisson ratio of 0.46. Here, NLpT denotes the number (N) of beads, dimension (L) in the x-direction, pressure (p) in the y- and z-directions, and temperature (T). We considered uniaxial elongating simulation with Poisson ratio 0.40 is suitable in order to understand basic behaviors and develop framework for systematic analyses of filled polymer materials. The value 0.40 can be regarded as central value of filled polymer materials. Poisson ratio of filled rubber and unfilled rubber is 0.46 and 0.49, respectively. Poisson ratio of crystalline polymer are smaller than that of rubber like polymers. Poisson ratio of polystyrene and high density polyethylene is 0.33 and 0.37, respectively. In our simulations, the elongation ratio λ is less than 400%. In the present paper, the elongation ratio λ is defined as the dimensions for λ becoming $(1 + \lambda)$ times that before deformation. In actual PNCs, the Poisson ratio is near 0.46, and nanovoids are considered to be observed for an elongation ratio much larger than 200% [13].

In the next section, the methods for cgMD simulation are explained. Stress-strain relations, and snapshots of nanovoids and fillers are presented in Section 3. Mathematical analyses of Betti numbers on the basis of computational homology are given. In the final section, a summary and conclusion are provided.

2. Methods

We used polymer networks filled with spherical NPs on the basis of the Kremer-Grest model [15]. The details of this model have

previously been explained [14]. Dynamics of the particles of polymer networks and NPs are described with a Langevin equation. For polymer networks, Lennard-Jones potential and the finite extensible nonlinear elastic (FENE) potential is applied to neighboring particles and bonded particles, respectively. For a model of a spherical NP, we considered that a sphere consists of the same beads as those of polymer chains and forms a fullerene structure C_{20n^2}. In order to make the NP spherical, a harmonic potential is applied to the surface particles from the center of the NP. The system size under a periodic boundary condition (PBC) is smaller than that in previous large-scale cgMD simulations [14]. In the present paper, the number of beads in the polymer parts is 655,360, which is composed of 640 chains with 1024 beads per chain. We used a smaller filler than that in the model proposed in previous studies. The filler consists of 320 surface beads and one center bead. The diameter of the filler is about 5.56 σ and the number of fillers is 256. The volume fraction of the NPs is about 20%. Thus, the dimension of the PBC box, L_{pbc}, before elongation is about 98 σ. It should be noted that the detailed values of L_{pbc} depend on the interaction parameters. In the present work, to create an attractive interaction among polymers, the cutoff length r_c of the Lennard Jones (LJ) potentials is set to 2.5 σ as shown in Table 1. The other parameters are the same, except for the interaction between NPs and polymers. The potential function for the interaction of the NP-polymer and NP-NP interactions is given as following function:

$$U_{NP-X}(r) = 4\varepsilon_{NP-X}\left[\left(\frac{\sigma}{r - r_{const}}\right)^{12} - \left(\frac{\sigma}{r - r_{const}}\right)^{6}\right.$$
$$\left. - \left(\frac{\sigma}{r_c - r_{const}}\right)^{12} + \left(\frac{\sigma}{r_c - r_{const}}\right)^{6}\right]. \quad (1)$$

Here, constant parameters r_{const} for the NP-polymer and NP-NP interactions are set to $r_{const,NP-P} = 0.25$ σ and $r_{const,NP-NP} = 0.0$ σ, respectively, for all cases. In order to compare the behavior during the creation and evolution of nanovoids, the interaction between NPs and polymers is set to repulsive and/or attractive, as shown in Table 1. As the solver of the cgMD simulation, we used a parallelized version of OCTA/Cognac Ver. 7.1 [16,17].

In the product runs, we deformed the PBC box in a uniaxial direction (the x-direction) with an elongation speed of 0.002 [1/τ]. The dimensions of the PBC box are $L_{pbc,x}(\lambda) = (1 + \lambda)L_{pbc,x}(\lambda = 0)$ for the elongation ratio λ. For a Poisson ratio of 0.4, the dimensions $L_{pbc,y}(\lambda)$ and $L_{pbc,z}(\lambda)$ in perpendicular directions are $L_{pbc,y}(\lambda) = (1 + \lambda)^{-0.4}L_{pbc,y}(\lambda = 0)$ and $L_{pbc,z}(\lambda) = (1 + \lambda)^{-0.4}L_{pbc,z}(\lambda = 0)$, respectively. Note that a Poisson ratio of 0.4 is smaller than that of actual PNCs (0.46) in order to develop analysis methods in advance of large-scale cgMD simulations. We considered a Poisson ratio of 0.4 to be reasonable to consider analyses of cgMD simulations of elongated PNCs.

We prepared the initial configurations for cgMD simulations as follows: The positions of nanoparticles are given by a certain hard sphere configuration. This corresponds to a well-dispersed configuration. We set polymer melts of 640 chains of $N = 1024$ segments per chain in the space, except for the NPs in the box under the PBC. Here, we performed Monte Carlo simulation of bond fluctuation model (BFM)[18] with adding new segment to both ends until number of segments in a chain becomes $N = 1024$, where used initial configuration is randomly distributed trimers [19,20]. The reason of use of the BFM simulation for the case with existence of NPs is that double bridge method [21–23] is out of scope because target value of end-to-end length of phantom chains cannot be determined. For the case without NPs, mean square internal distance (MSID) from the BFM is similar to that of long cgMD runs by