Coarse-grained Molecular Dynamics Simulation Approach for Polymer Nano-Composites Rubber

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Abstract

We examined dynamics of entangled long-polymer melts and filled polymer rubber by using coarse-grained model. We confirmed that reptation behaviors \( \tau \propto N^{3.4} \) and \( D \propto N^{-2.4} \) observed in experiments can be reproduce by on-lattice Monte Carlo simulation using bond fluctuation model, where \( \tau \) is the longest relaxation time of a chain, \( D \) is the self-diffusion constant of the center of mass of a chain, and \( N \) is number of segments per a chain. By using coarse-grained molecular dynamics (MD) simulations based on Kremer-Grest model, we can examine dynamics of polymer nano-composites consist of polymers and fillers such as carbon black and clay. We developed coarse-grained model of a filler which can be defined by segments and bonds of Kremer-Grest model in consideration of reproduction of inertial momentum. We also implemented purely massive parallel code for MD simulation of polymer nano-composites. It is found that the presented model of a polymer nano-composite of tire rubber can reproduce almost of feature of the reinforcement effect observed in experiments. We confirmed that rheological properties, loss tangent \( \tan \delta \), can be estimated from relation between stress and strain under oscillating deformation, where \( \tan \delta \) is widely used as one of index of energy loss of tire rubber.

1 Introduction

Prof. Ryogo Kubo gives us area of polymer physics (soft matter physics) as statistical physics starting from his Ph. D. thesis and the great book “Rubber elasticity”[1] written in the his 20s before the kubo thoery. (This great book is republished and loved by current rubber researchers, including industrial peoples, as the textbook of polymer physics.) Rubber like behavior of entangled long-polymer melts has been examined by many experiments. Behaviors of longest relaxation time \( \tau \propto M^{3.4} \) of a polymer chain and self-diffusion constant \( D \propto M^{-2} \) of center of mass of a polymer chain is well known[2, 3], where \( M \) is molecular weight of a polymer chain. (Recently, behavior of \( D \) has been revised as \( D \propto M^{-2.4}[4, 5] \).) In the 1970s, Prof. P. G. de Gennes, Sir. S. F. Edwards, and Prof. Masao Doi proposed reptation theory and Doi-Edwards theory in order to describe this slow dynamics of entangled long polymer melts[2, 3]. It is believed that this discrepancy between experiments and theory can be understood by the contour length fluctuation[3]. About 30 years ago, Prof. K. Binder raised the challenging problem, that is, the confirmation of the behaviors of \( \tau \) and \( D \) by Monte Carlo simulation and/or molecular dynamics (MD) simulation without assumption of reptation behavior[6]. In this century, the authors[10, 11] have presented first simulation results consistent with \( \tau \propto N^{3.4} \) and \( D \propto N^{-2.4} \) by using bond fluctuation model, where \( N \) denotes number of segments per a chain.

Polymer nano-composite materials are widely used in our daily life. Improvements by nano science and technology are required in order to emerge new functions and to contribute Green Innovation. Recently, synthesis method of a non-linear polymer, which has a complex architecture, has been developed. Dynamics and rheology of star polymers and non-linear polymer which has complex architecture are examined[7, 8]. We can see applications of
star polymers and non-linear polymer in released polymer materials. Recently, Prof. D. Richter’s group focus on polymer dynamics confined between fillers in a bulk of polymer nano-composites (tire rubber) by neutron experiments[9]. MD simulations of polymer chains is expected to understand mechanism of the behavior of such a non-linear polymer and confined polymers. Although computing costs for MD simulations to examine dynamical and rheological behavior are huge, recent top supercomputers have enough powers to perform them. It becomes time to try these problems and extend to applications.

2 Entangled long polymer chain melts

In recent years, the slow dynamical behavior of a polymer chain in a melt is confirmed by many simulation studies[6, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. These studies tried to clarify the behaviors of the longest relaxation time and self-diffusion constant $D$ are consistent with the experimental results $\tau \propto N^{3.4}$ and $D \propto N^{-2.4}$, where $N$ means the number of segments of a polymer chain[2, 3, 4, 5]. This slow dynamics can be roughly understood by reptation theory ($\tau \propto N^3$ and $D \propto N^{-2}$). It is believed that the discrepancy between experiments and theory is clarified by bead spring model which is independent from chemical details. We reviewed our simulation study of entangled long polymer chain melts[10, 11] as follows.

2.1 Reptation theory

In the reptation theory[2, 3], the dynamics of concentrated polymer chain system is described in terms of the motion of a polymer chain trapped in a tube (primitive path), which represents the entanglement effects of the surrounding polymers. The polymer chain trapped in a tube is considered to the sequence of the blob, the diameter of which is about the tube diameter. Then, the polymer chain consists of $N/N_e$ blobs, where the blob consists of $N_e$ segments. The longest relaxation time, the self-diffusion constant, and the dimensionless parameter $D\tau/(R_e^2)$ are predicted to show $\tau \propto N^3/N_e^2$, $D \propto (N_e/N)^2$, and $1/(3\pi^2)$, respectively. Although the discrepancy of the $N$-dependence of the longest relaxation time $\tau$ between theoretical and experimental results is considered to be attributed to the contour length fluctuation[22, 23, 24, 25]. The contour length fluctuation makes the slowest relaxation time $\tau$ shorter than the predicted by the original reptation theory. As results, it is believed that $\tau \propto N^{3.4}$ due to finite polymer chain length treated in experiments.

2.2 Bond fluctuation model

In this study, we used the bond fluctuation model[26] for Monte Carlo simulations of a polymer melt. A system of $M$ polymer chains, each of which consists of $N$ segments, is considered on a simple cubic lattice of which the lattice constant is $a$. Each side of the lattice has $L$ lattice points and the periodic boundary conditions are applied. The polymer chains are represented by $M$ series of $N$ lattice points $f(r_1;m; r_2;m; \ldots; r_N;m)$, where $r_i;m$ denotes the center of the $i$th segment of the $m$th polymer chain. Each segment occupies a cube of $2^3$ unit cells and no overlap of segments is allowed. The volume fraction is given by $\phi = 2^3MN/L^3$. The lengths of the bond vectors are restricted to the five prescribed lengths $\{2a, \sqrt{5}a, \sqrt{6}a, 3a, \sqrt{10}a\}$. The center of each segment stochastically moves to one of its nearest neighbor lattice points with the transition probability per unit time $\gamma/6$ if the new position is allowed by the conditions for the excluded volume and the bond vectors. The dynamics is simulated by a standard Monte Carlo method, which uses discrete time steps and updates $MN$ segments in random sequence. The time scale $\gamma^{-1}$ corresponds to one update per segment. We choose $a = 1$ and $\gamma = 1$.

2.3 Relaxation Modes Analysis

Relaxation modes and rates are given as left-eigenfunctions and eigenvalues of the time-evolution operator of the master equation of the system, respectively[10, 27, 28, 29,
In order to solve a variational problem equivalent to the eigenvalue problem approximately[27, 28], we choose a trial function for relaxation modes as $X_p = \sum_{i=1}^{N'} f_{p,i}^{(n)} (t_0 + t_1) \mathbf{R}_i^{(n)}$ with $N' = N/n[32]$. Here, $A(t; Q)$ represents the expected value of quantity $A$ after period $t$ starting from configuration $Q$ of the system. The quantity $\mathbf{R}_i^{(n)}$ denotes the position vector of the $i$th coarse-grained segment of a polymer chain relative to its center of mass: $\mathbf{R}_i^{(n)} = \frac{1}{n} \sum_{k=1}^{n} \mathbf{R}_{i(k)+n+k}$ with $\mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_c$ and $\mathbf{r}_c = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i$. Hereafter, the index indicating a polymer chain is omitted from the subscripts, because we are interested in the relaxation of the relative positions of the segments of the same polymer chain. For the trial function, the variational problem becomes the generalized eigenvalue problem $\sum_{j=1}^{N'} C_{i,j}^{(n)} (t_0 + t_1) f_{p,j}^{(n)} = -\lambda_p^{(n)} \sum_{j=1}^{N'} C_{i,j}^{(n)} (t_0) f_{p,j}^{(n)}$ for the equilibrium time correlation matrices $C_{i,j}^{(n)} (t) = \frac{1}{3} (\mathbf{R}_i^{(n)} (t) \cdot \mathbf{R}_j^{(n)} (0))$ with the orthonormal condition \( \sum_{i=1}^{N'} \sum_{j=1}^{N'} f_{p,i}^{(n)} C_{i,j}^{(n)} (t_0) f_{q,j}^{(n)} = \delta_{p,q}[10, 27, 28, 32] \). The variational parameters $f_{p,i}^{(n)}$ and the corresponding relaxation rate $\lambda_p^{(n)}$ are determined as the solutions of the generalized eigenvalue problem. The solutions $f_{p,i}^{(n)}$ and $\lambda_p^{(n)}$ are numbered from $p = 1$ to $p = N' - 1$ in increasing order of the relaxation rate $\lambda_p^{(n)}[28]$. The contribution of the $p$th slowest relaxation mode to $\mathbf{R}_i^{(n)}$ is given by $\gamma_{p,n} = \exp(-\lambda_p t_0/2) \sum_{j=1}^{N'} C_{i,j}^{(n)} (t_0) f_{p,j}^{(n)}[10, 27, 28, 32]$.}

2.4 Results

In the references 10 and 11, the results for $\phi \simeq 0.5$ are presented. Figure 1 shows a log-log plot of $\tau/N^2$ versus $N$ and $1/(DN)$ versus $N$. Here, the self-diffusion constant $D$ is estimated by fitting the data points at times longer than the longest relaxation time $\tau$ to a straight line $\langle (\mathbf{r}_c(t) - \mathbf{r}_c(0))^2 \rangle = 6Dt + \text{constant}$. From the data for $N = 256, 384$ and $512$, the apparent exponents $x_t$ and $x_d$, which describe the power law dependences of $\tau$ and $D$ on $N$ as $\tau \propto N^{x_t}$ and $D \propto N^{-x_d}$, are estimated to be $x_t \simeq 3.5$ and $x_d \simeq 2.4$, respectively. These exponents for $\tau$ and $D$ agree with the experimental results $\tau \propto N^{3.4}[2, 3]$ and $D \propto N^{-2.4}[5]$, respectively. The reptation theory predicts that the ratio $D\tau/(R^2_t)$ is independent of $N$ for sufficiently large $N$, where $\langle R^2_t \rangle$ denote the mean square end-to-end distance of a polymer. Moreover, the apparent exponent of the power law dependence $\langle R^2_t \rangle \propto N^{2x_t}$ has been estimated to be $2x_t \simeq 1.0$ for $N = 256, 384$ and $512[10, 11]$. Thus, it seems that the relation $-x_d + x_t - 2\nu \simeq 0$ holds, which means that $D\tau/(R^2_t)$ is independent of $N$ even in the range of $N$ where the theoretical asymptotic behaviors of $\tau$ and $D$ are not seen. According to the reptation theory, the ratio $D\tau/(R^2_t)$ is a constant value $1/(3\pi^2) \simeq 0.034$, which contains no adjustable parameter[3]. It has been found that $D\tau/(R^2_t)$ seems to converge to a constant value around $0.024$ for $N \geq 192[11]$. This value reasonably agrees with the value predicted by the reptation theory, if this value can be regarded as the large $N$ limit of $D\tau/(R^2_t)$. Although the detail is not presented, this behavior seems to hold for $\phi \simeq 0.375$ and $0.625$.

2.5 Conclusion

We can reproduce the reptation behavior observed in experiments by on-lattice Monte Carlo simulation using bond fluctuation model.
corresponding to spring bead model. The challenging problem raised by Prof. K. Binder has been closed. This result gives assurance to reproduce the reptation behavior by coarse-grained MD simulation. Moreover, it is expected that many physical properties of entangled long-polymer system including polymer nano-composites rubber can be estimated by coarse-grained MD simulations.

3 Polymer nano-composites rubber

Recently reinforcement effect of polymer nano-composites rubber has been attracted much interest from the viewpoint of polymer physics and nano-science as well as engineering applications[33]. It is well known that rubber materials used in daily life consist of many raw materials and are processed in complicated ways. These manufacturing methods are realized by much trial and error without understanding detail mechanism. Empirically, we know that macroscopic behavior for engineering products can be understood as continuum mechanics and material chemistry which works as modification of atomic level interactions. However, it has been considered to be too hard to understand behavior of polymer nano-composites rubber from molecular (nm scale) level as a problem of physics. Recently, we show a possibility of molecular-level understanding dynamics and mechanics by using coarse-grained MD model of filled polymer such as tire rubber. Brief reviews of current studies are presented as follows.

3.1 History of improvement of tire rubber material

From viewpoint of polymer physics, it can be considered that tire rubber has been improved by three serendipitous discoveries as follows. First discovery is process for vulcanization of rubber. It is discovered by C. Goodyear in 1839. Chemical crosslink between polymer chains with addition of sulfur makes solid like rubber from liquid like one. Second one is a reinforcement effect by addition of carbon black to rubber. In 1904, S. C. Mote found that the addition of carbon black enhanced tensile strength of rubber. It is known that diameter of carbon black particles which show the reinforcement effect are from 10 nm to a few 100 nm and the reinforcement effect becomes particular in the case that volume fraction of carbon black is above percolation threshold (about 20%) for its electric conductivity[33]. According to recent experimental studies of tire rubber composites, we found that the effect of filler morphology on dynamical properties is not small[33, 34]. These facts emerge that polymer chains, crosslink, and fillers have important roles on basic properties of rubbers composites and scale relation of entanglement length of polymer chain, distribution of crosslink, and size and structure of fillers are essential. Third discovery is improvement of the reinforcement effect by addition of silica nano-particles with coupling agent which makes a chemical bond between polymer chains and silica nano-particles. In the late 1990s, Michelin company makes first commercial tire products filled with silica nanoparticles. The addition of silica nano-particles improves dynamical properties of rubber composites and reduces rolling resistance of tire as a result. It is expected that a polymer chain grafted on a filler yields drastic changes on dynamical properties[34].

3.2 Kremer Grest model

Kremer Grest (KG) model[14] consists of simple potentials and Langevin dynamics using random forces. A potential among all segments is given by repulsive part of Lennard-Jones (LJ) potential.

\[ U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] \]  

for \( r \leq 2^{1/6}\sigma \) and \( U_{LJ}(r) = 0 \) otherwise. Here, \( r \) is a distance between two segments, \( \epsilon \) is a parameter of an interaction and \( \sigma \) is a size of the excluded volume. It is noted that usual LJ potential \( U_{LJ}(r) = 4\epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right] \) with attractive part should be used in order to study behaviors in the region of glass transition and glassy state in spite of larger required computing costs. A bond potential between neigh-
boring segments on a chain is given by Finite
Extensible Non-linear Elastic potential:
\[ U_{\text{FENE}}(r) = -\frac{k}{2} R_0^2 \ln \left(1 - \frac{r^2}{R_0^2}\right), \tag{2} \]
where \( r \) is a distance between neighboring segments, \( k \) is a spring constant and \( R_0 \) is maximum length of the spring. We use \( m = \sigma = \epsilon = \gamma_{\text{MD}} = 1, \) \( \zeta = 0.5 \sigma \gamma_{\text{MD}} / \sigma, \) \( k \sigma^2 / \epsilon = 30, \) and \( R_0 / \sigma = 1.5. \) We have simulated an NVT ensemble by using Langevin dynamics at \( k_B T = 1.0, \) where \( k_B \) is Boltzmann\'s constant. The fluctuation-dissipation relation for the random forces is described as \( \langle f_{i,\alpha}(t)f_{j,\beta}(t') \rangle = 2\gamma k_B T \delta_{i,j} \delta_{\alpha,\beta} \delta(t - t'), \) where \( f_{i,\alpha} \) is a random force of \( i \) th segments in the \( \alpha \)-direction and \( \gamma \) is a friction coefficient. In the present study, the time evolution of positions and velocities of all segments are obtained by the velocity Verlet integrator with \( \gamma = 0.5 \) and time step \( \Delta t = 0.005. \)

3.3 Coarse-grained model of filled rubber

According to the history presented above and experimental facts, it is considered that important elements of tire rubber for mechanical function (excluding process for fabrication) are long polymers, fillers, crosslinks, and grafted polymers. We consider a simple model of rubber composites to capture essential properties as follows. Rubber consists of entangled polymer chains is given by KG model [14]. According to the reference [14], a polyisoprene of 100k molecular weight corresponds to a chain consists of about 1k particles of KG model. Here, 100k molecular weight is considered as a condition to make the real rubber products[33, 34].

In general cases, shape of filler is near to sphere. According to experiments, effect of inertial momentum on behavior of stress-strain relation is not negligible. It simple large spheres are used, implementation to treat inertial moment is required in addition to usual MD algorithm and becomes a limiting factor of parallelization. Because MD simulation of more rigid aggregates required shorter time steps, we want to avoid such a hard computing and to use clever equivalent mechanical model.

We proposed a following model of fillers. It is assumed that filler is sphere and described by icosahedral fullerene structure with a repulsive force from the center of the filler to the surface particles. Here, the surface particles and bonds of the fillers are given by the same model as the polymer chains. We also considered conservation of inertial momentum of fillers by reweighting mass from center to surface particles. We remain a freedom related to interaction between polymers and fillers due to empirical facts. For the case of LJ attractive interaction between fillers and polymers, we use a shifted LJ potential
\[ U_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r - \sigma/4} \right)^{12} - \left( \frac{\sigma}{r - \sigma/4} \right)^6 \right] \tag{3} \]
to avoid that polymer chain penetrates into inside of icosahedral fullerene structure, because center of hexagon of surface particles of a filler becomes most attractive point.

For simplicity, we use a bond of KG model as a model of crosslink which means a bridge between chains. A grafted chain on fillers can be prepared by putting a bond between a particle of a chain and a surface particle of a filler.

3.4 Purely massively parallel computing for coarse-grained MD model of polymer/filler system

We developed an implementation of purely massive parallel code of MD simulation of long entangled polymer melts. For polymers, the force along polymers is computed in addition to the non-bonding force among near particles. Usually, for large scale MD simulations, spatial or particle decomposition method is applied only for calculation of the non-bonding force. The force along polymers is calculated after exchange of all data among all threads. For a larger scale, ex. billion atoms with 4000 threads, it is difficult to gather all data or exchange data among all threads. Locality is important for scalability of memory and computation. For polymer systems the size of overlapping area among neighboring threads becomes 3 times larger than that of simple particle systems due to interaction along polymers. The maintenance of information of polymer
connectivity is also complicated. Our code shows good parallel efficiency for 0.13 billion atoms with 4096 MPI threads on Earth simulator and over 32000 MPI threads are allowed according to estimation[35].

For an extent for polymer/filler systems, we also applied a custom implementation in order to keep locality of the data and fast computing. In our implementation, positions, velocities, and sum of force of center of all fillers are communicated at the same time when summation of kinetic energy and temperature by using one ”MPI Allgather” call function per a MD step. When the data of positions of fillers exist on MPI process, we can compute a force between a particle of a polymer in a spatial decomposed box and a center of a filler out of a overlapping area of this MPI process as shown in Figure 2. Although little memory and computing time for update of positions of center of fillers are duplicated across all MPI process, we can reduce communication times to almost minimum. It is noted that an answer for invariance among computing costs of each MPI thread is important for high efficient parallel computing. Study for this direction is in progress.

3.5 Two-dimensional reverse Monte Carlo method

In order to perform coarse-grained MD simulation, an initial position of fillers is considered to be important according to experimental knowledge. Unfortunately, there is no method of direct measurement of positions of fillers in a bulk[34]. (Although some methods for ultra thin film and/or surface exist, it is hard to observe dynamical behavior under deformation.) However, we can get information of behaviors of fillers in elongated rubbers by X-ray and neutron scattering experiments. Shinohara et. al. have performed two-dimensional ultra-small-angle x-ray scattering (2D-USAXS) experiments to observe structural changes of spherical silica particles in elongated rubbers by using the Beam line BL20XU of SPring-8 (Hyogo, Japan) [36]. In order to estimate three dimensional structures of fillers from obtained two dimensional scattering patterns on reciprocal space, we have developed an extended version of reverse Monte Carlo (RMC) analysis, which is called two-dimensional pattern RMC [37, 38, 39]. Reverse Monte Carlo analysis is widely used as a general method for the diffraction data analysis for disordered materials [40]. The details of the method have been described in the early works [41, 42, 43]. It can model three-dimensional structure in a real space, that is, atomic configurations from a measured structure factor. Actually it iteratively replace the atomic configuration so that the difference between observed and calculated structure factors is minimized within the errors. Although it seems to sound to be easy, computing costs for the case of two-dimensional scattering patterns are not small. Therefore, in order to reduce computing costs, we assume $x$-$y$ ($q_x$-$q_y$) symmetry perpendicular to elongating direction ($z$-axis). Here, this assumption is confirmed by our custom-made experiments [44]. In actual computing, we calculate intermediate functions in two dimensions by azimuthally average of obtained (three dimensional) pair distribution function over the $x$-$y$ plane and two-dimensional scattering patterns are calculated from this intermediate functions. This approximation and
computing power by supercomputers at ISSP and Earth simulator can put two-dimensional pattern RMC method into realization. Although details is not presented in this paper, we have been reproduced configurations during the elongation from elongation ratio 0% to 150% [37, 38, 39].

In addition to this method, we have also developed the extended method of 2D pattern RMC for multiple two dimensional scattering patterns in many directions of X-ray beam in order to study bicontinuous structure such as a double gyroid structure [45]. These methods are only for structure factor $S(q)$ of monodisperse spherical filler particles of a certain diameter. When the distribution of diameters of particles is polydisperse, we should estimate from $I(q)$ instead of $S(q)$. It is considered that polydispersity of filler particles is important for their morphology of filler particles and dynamical properties of filled rubber composites. For simplicity, we assume that the diameter distributions of spherical particles are given by size distribution histograms observed in experiments. $I(q)$ can be calculated from size distribution histograms, form factors of a spherical particle, and positions of particles. The method for polydisperse case is under development.

### 3.6 Rough estimation of effective crosslink density

In the present time, it is hard to estimate effective crosslink density due to lack of a direct measurement method. This problem is also related to nature of entanglement in polymers. In practice, a value of effective crosslink density is estimated by swelling experiments using toluene with assumption of ideal endlinked gels[46]. It is well known that the obtained value is far from a value estimated from amount of sulfur and a probability making a crosslink by a sulfur. According to an expert comment by a tire company, it is considered that effective crosslink density is $4.0 \times 10^{-5}$ mol/cm$^3$ for 0.5g sulfur atoms per 100g rubbers (0.5phr)[34]. Thus, we emulate this swelling experiment by zero pressure NPT simulation of coarse-grained MD model of crosslinked polymers corresponding to the crosslink density $4.0 \times 10^{-5}$ mol/cm$^3$. The obtained expansion coefficient seems to roughly agree with experimental ones. It should be noted that $\chi$ parameter between toluene and polymers is important to swelling feature although it is not taken into account. Detail examinations and improvements of this method are in progress. In addition, distribution of sulfur is unknown still. A method for it using EXAFS experiments and etc. is under construction[34].

### 3.7 Results for constant elongation

We presented a preliminary result of large scale coarse-grained MD simulation of filled polymer melts with sulfur-crosslink under an uni-axial deformation. In the present study, we set diameter of a filler to about 15nm. The size of simulation box under periodic boundary conditions (PBC) is set to about 66nm to consider length of entangled polymer chains, size and structure of fillers, and non-uniform distribution of crosslink. We put 640 polymer chains of 1024 particles and 32 fillers into the PBC box. One filler consists of 1280 particles of the C$_{1280}$ icosahedral fullerene structure which corresponds to a filler of 15nm diameter. The distribution of the fillers used in this simulation is a part of configuration obtained by 2d pattern RMC analysis for 2D-USAXS experiments at SPring-8. Sulfur crosslink are randomly distributed in the system. In simulation, we elongate the system with a speed $4 \times 10^{-4}$%/MDsteps (0.8%/1nsec) in the $x$-direction by using assumption of the affine deformation. Figure 3 shows a snapshot of elongated filled polymer rubber. It is found that stress-strain curves estimated by applying the uni-axial deformation to the system in simulations are in good agreement with those in experiments. Figure 4 shows stress-strain (S-S) curve of filled rubber and unfilled rubber under elongation. It is successful to show difference on the S-S curve between existence / absence of fillers by using same parameter to determine force unit. Although details are not presented here, we confirmed the qualitatively agreement with experiments for effects of poly-
3.8 Preliminary study of rheological properties

Recently, we examine rheological properties of polymer network gel confined by two parallel walls using coarse-grained MD simulations of KG model[47]. We use end-link gel, which forms simple cubic lattice, under PBC in x- and y-directions as model of the polymer network gel. The two walls are perpendicular to the z-direction. Interaction between walls and polymers is much attractive to avoid to slip at interface between walls and polymers. The end-link gel is compressed and equilibrated at number density same as simulations of entangled polymer melts. We study dependencies of the deformation of the polymer network gel on the wall moving only in x-direction under oscillating shear where a strain $\epsilon(t)$ is described by $\epsilon(t) = \epsilon_0 \sin(\omega t)$. Viscous modulus, elastic modulus and loss tangent ($\tan\delta$) are usually used to evaluate viscoelastic properties. Here, loss tangent is defined as the ratio of viscous modulus to elastic modulus. Actually, $\tan\delta$ is given by the tangent of the phase angle $\delta$ of the observed stress $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$. We demonstrated how we can estimate values of $\tan\delta$ from results of coarse-grained MD simulations under oscillating shear. It is also confirmed that attractive part of Lennard Jones potential among segments needs to simulate glass transition region and only repulsive part is good to simulate rubber-like region. We also found indications that grafted chain on walls give singular effect for viscoelasticity.

We also applied this scheme under oscillating shear to filled polymer system in order to estimate rheological properties. For a preliminary study, we examined 4 fillers system, whose size of a PBC box is about 33nm. There are 80 chains and 4 fillers in the PBC box. Although a detail is not presented here, we obtained good results to predict rheological properties and design tire performance for the grip and breaking region[34].

3.9 Conclusion

We developed coarse grained MD model of tire rubber and confirmed its validity at least qualitatively. It is found that the rheological properties related to product performances can be predictable. It is expected that some innovations of tire products and progresses of polymer science are provided by using next generation supercomputer at Kobe.
4 Summary

It is confirmed that reptation behavior observed in experiments can be reproduced by coarse-grained model without chemical details. Recently, we found that dynamics properties of tire rubber can be reproduced by using coarse-grained MD simulations. We expected that coarse-grained MD technique for polymer nano-composites can be applied for frontier of nano-technology to develop advanced polymer material. It will lead to achievement of one of Green Innovation.

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