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Influence of Filler Dispersion on Mechanical Behavior with Large-Scale Coarse-Grained Molecular Dynamics Simulation

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Filler morphology impact the physical properties of filled rubber. Two large-scale coarse-grained models containing 1,000 filler particles and 20,000,000 polymer beads were created and coarse-grained molecular dynamics simulations based on Kremer-Grest model were carried out in order to investigate a relationship between filler morphology and mechanical behavior. One is an aggregated model including a non-homogeneous filler distribution which is determined by TEM image analysis, and the other is a uniformity arranged model in which filler particles are distributed in lattice pattern. Comparing stress-strain curves of both models under cyclic deformation stretching to $\lambda = 2.0$, we confirmed that effects of filler morphology observed in experimental results were reproduced qualitatively by our simulations. The effects of filler morphology are differences of mechanical behavior, modulus and hysteresis of the aggregated model are greater than the uniformity arranged model and that remains in subsequent cycles. Analyzing stresses of both models, we found the differences are mainly attributed to filler stress induced during deformation. Fillers are to be contacted with another adjacent filler particle during deformation and filler stress grows when fillers are aggregated. In addition, differences in contact direction of fillers between loading and unloading increase hysteresis of the aggregated model. Breakage of filler aggregate due to the contacts between fillers in the 1st loading causes stress-softening as contact force and area decrease. We focused on changes of length of polymer-paths bridging filler particles and measured those in the uniformity arranged model in order to study a origin of stress which result from polymer chains dynamics. It was found that polymer-paths become longer to adjust the increase of filler-filler distance particularly in the 1st loading, and the change of polymer-paths in subsequent cycles are lesser than the 1st loading. This irreversible change of polymer network causes hysteresis and stress-softening derived from polymer dynamics.

1 Introduction

Tyre labeling has become widespread and tyre manufactures have focused on development of tyre performance, such as rolling resistance, wear, and wet traction. To improve tyre performance, it is necessary to improve mechanical properties of filled rubber(Wang et al.(1998)). Exploration into new silane coupling agents and development of modified polymer chain end have be made in the last few decades (B.T.Poh et al.(1998), T.Sone et al(2010)). For material design processes, it has been a subject of very considerable interest that studies not only based on experiments but also by using high performance computer, such as numerical simulations based on the continuum mechanics of filler and rubber composites with the aim of reducing energy dissipation (H. Kishimoto et al. (2013), Bauerle et al. (2004), M.Koishi et al. (2010), C.T.Wu et al. (2012), B. Figliuzzi et al. (2016), R. Dargazany et al. (2009)). These simulations, based on the continuum mechanics, require a constitutive equation to reproduce mechanical behaviors, and have allowed studies on the impact of filler structures. However, it is difficult to investigate dynamics of a discontinuous microscopic structure, i.e. dynamics of polymer chains, directly; in other words, it is difficult to determine origin for mechanisms of the characteristic behavior, e.g. hysteresis, and stress softening, of filled rubber. In order to understand the mechanisms of these properties, Coarse-Grained Molecular Dynamics simulation(CGMD), which provides a simulation at a finer level than continuum simulations as typified by FEM, is suitable for a simulation of polymer chain dynamics.

CGMD have been frequently performed to know relationship between nano-structure of filled rubber, e.g. entanglements of polymer chains, cross-linking, modified polymer chain end, variety of nano-particle, and dynamic viscoelastic properties, and dynamics of polymer chains in the vicinity of filler during deformation (Y.Masubuchi et al (2001),S.Kalpana et al (2006),H.Yagyu et al (2009), G.Raos et al (2011),A.A.Gavrilov et al. (2014)). We have stud-

ied mechanisms of the mechanical behavior of filled rubber with small-scale CGMD of 4 filler particles(T.Kojima et al.(2016)). Change of polymer density induced by adding fillers and creating of irreversible change of polymer conformation between fillers during the deformation (Bueche et al (1960),Dannenberg et al (1975),Rigbi et al(1980)) are major reasons of reinforcement effect by adding fillers, hysteresis, and stress-softening well known as Mullins' effect (Mullins (1948)).

It is well known that filler morphology impact on the mechanical behavior (G.Kraus et al (1966)) as shown in Figure 1 which provides experimental results of two samples with different filler morphology. TEM images of both samples are given in Figure 2. However, few studies address the impact of not only the filler morphology but the cyclic deformation. In the present paper, we sought understand a relationship between filler morphology and mechanical behavior under cyclic deformation using CGMD. First, we created two large-scale coarse-grained models; a uniformity arranged model in which filler particles were arranged in a lattice pattern and an aggregated model in which filler particles were arranged randomly based on TEM image analysis. After a two cycle deformation, we analysed the dynamics of polymer chains and change of filler morphorogy.

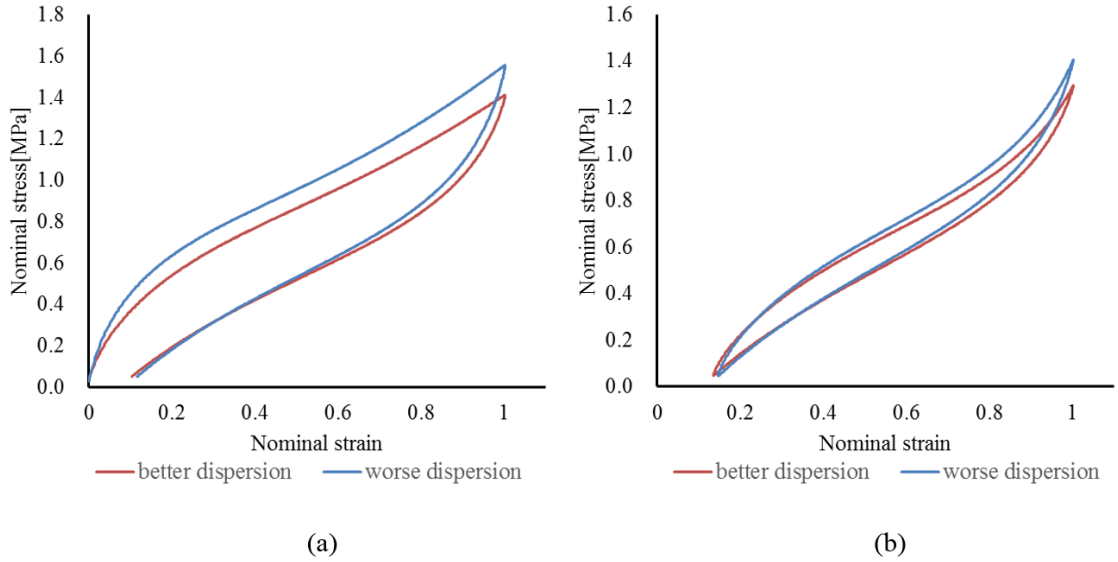


Figure 1: Measured stress-strain curves of better dispersion sample and worse dispersion sample:(a) 1st cycle; (b) 2nd cycle.

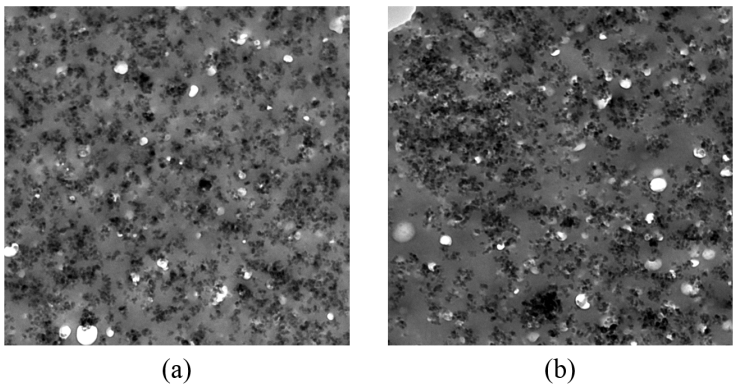


Figure 2: TEM images of filled rubber:(a) better dispersion sample; (b) worse dispersion sample.

2 Simulation Details

2.1 Polymer Models

We employed the Kremer-Grest model (K.Kremer et al.(1990)) for a modeling of polymer chains. A polymer chain model consists of 1,000 bead-necklace chains of length 20,000 beads and includes 60,000 cross-linking bonds, and polymer beads are distributed at density 0.85 following the previous report (K.Kremer et al.(1990)). The cross-linking bonds were created by cross-linking reaction simulations -- simulations of sulfur vulcanization (G.Grest et al.(2000), T.Hayakawa et al.(2005), E.Duering et al.(1994)), which was conducted after putting filler particles into the polymer melt system. The interaction between polymer beads was modeled using Lennard-Jones potential as given by:

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

where ϵ and σ denote the strength of the interaction and the diameter of the shpere, respectively. The cutoff distance is the valid range of the interaction potential, in this study cutoff distance $r_c = 2^{\frac{1}{2}}$. This value means repulsive interaction.

The polymer chains connecting adjacent polymer beads is modeled using FENE_LJ potential as given by:

$$U_{bond}(r) = U_{FENE}(r) + U_{LJ}(r) \tag{2}$$

$$U_{FENE}(r) = -\frac{1}{2} k R_0^2 \ln \left[1 - \left(\frac{r}{R_0}\right)^2 \right] \tag{3}$$

where k, R_0, σ, and ϵ stand for spring constant, finite extended length, diameter of the LJ sphere, and strength of the interaction, respectively.

The interaction between a filler bead which constitutes a filler particle and a polymer bead was modeled by using the Lennard-Jones potential with cutoff distance $r_c = 2.5$. This value represents the attractive interaction which is the interaction between polymer and Carbon black (J.B.Donnet et al (1993),C.L.Mantell et al (1968)).

2.2 Filler Models

A filler was a solid particle combined beads by bonds, of which the radius was approximately $10[\sigma]$. 1,000 filler particles were put in each simulation box at 15[%] volume fraction. Here, the strength of the interaction ϵ was 15 to model strong interaction. Filler-filler interaction was also modeled by using the Lennard-Jones potential and cutoff-distance r_c was $2^{\frac{1}{6}}$, representing the repulsive interaction.

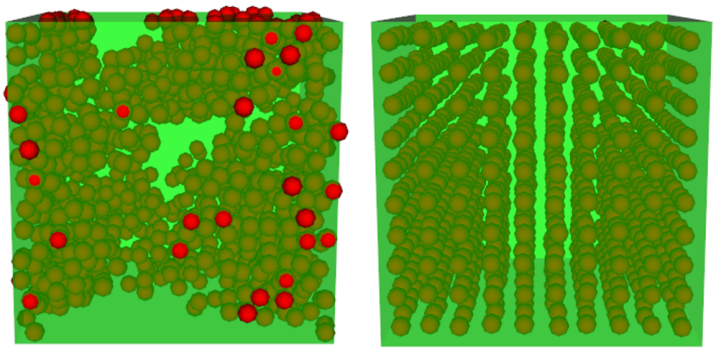
In the present paper, two models as shown in Figure3 were created. Filler positions of the aggregated model were determined by fitting from experimental covariance and cumulative granulometry obtained from TEM image analysis (D. Jeulin et al (2016)).

2.3 Simulation Procedures

The stress-strain responses were simulated under two cyclic uniaxial deformations stretching to a nominal strain of 1.0 at elongation velocity $0.01[\sigma/\tau]$. All simulations were carried out with COGNAC (Aoyagi et al (2002)) and VSOP (JSOL corp.). Figure 4 shows the sequence of process of our simulation.

3 Resluts of Cyclic Deformation Simulations

First, we explain the effect of filler morphology on the experimental data shown in Figure1. Famous features of filled rubber; hysteresis, stress-softening, and permanent set, are observed in both curves. Both the growth of stress in loading and the reduction of stress in unloading of the worse dispersion sample are greater than the better dispersion sample in both cycles, therefore hysteresis in the worse dispersion sample is greater.



(a) (b)

Figure 3: Filler positions for large-scale CGMD:(a) aggregated model, (b) uniformity arranged model. Red dots and green domain represent filler particles and polymer phase, respectively.

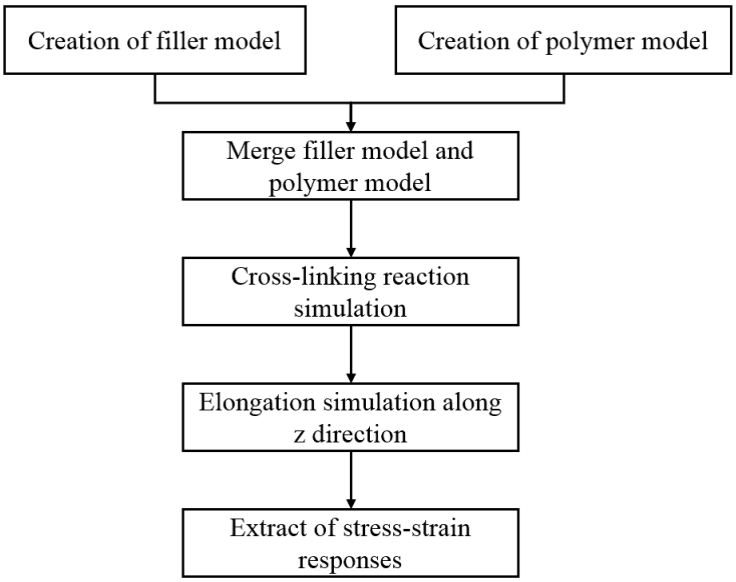
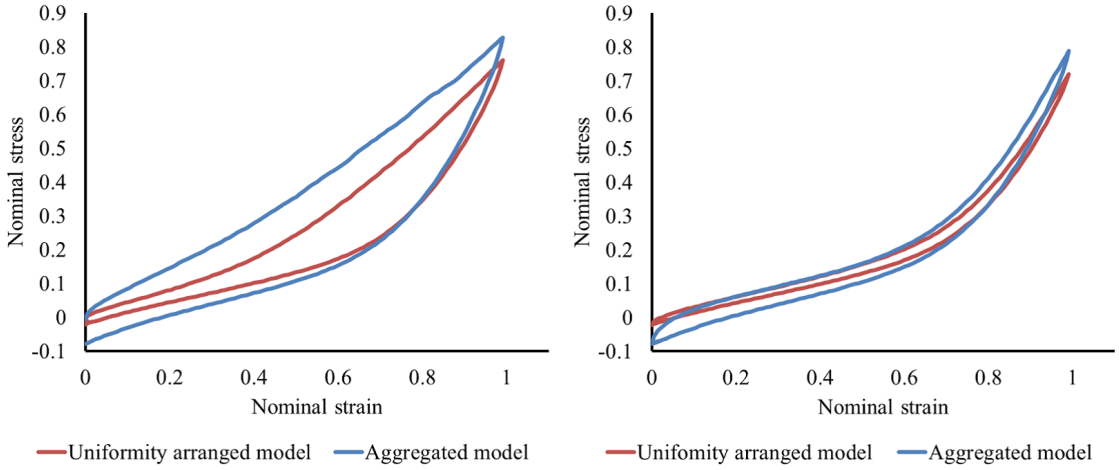


Figure 4: Simulation procedure.

Figure 5 shows the simulated stress-strain relations under 2 cycles. It is clear that not only characteristic behavior of filled rubber described above but also the effect of filler morphorogy are reproduced qualitatively.

We succeeded in reproducing the effect of filler morphology by putting 1,000 filler particles in the simulation box.



(a) (b)

Figure 5: Simulated stress-strain curves of the uniformity arranged model and the aggregated model:(a) 1st cycle; (b) 2nd cycle.

4 Decomposition of Stress

Stress of the system was decomposed into ”bond stress” and ”nonbond stress” in order to clarify the origin of the difference of mechanical behaviors impacted by filler morphology (see Figure 6). The bond stress and the nonbond stress arise from bond force/stretch and bond orientation, respectively. Not only hysteresis and stress-softening but also the difference of mechanical behaviors result from bond stress. As the 2nd step, bond stresses of both models were decomposed into ”polymer bond stress” and ”filler bond stress” to study the origin in detail (see Figure 7). Consequently, we confirmed the difference of the bond stress in filler phase results in the difference in responses of the systems, as there are clear differences in the filler bond stress.

The filler bond stress arises from deformation of fillers. Hence, it is implied that the difference in mechanical behavior results from the difference of filler deformation affected by filler morphology.

5 Contribution of Polymer to Mechanical behavior

We explain a mechanism of ”polymer bond stress” which is not much affected by filler morphology, while polymer bond stress is the basis of hysteresis and stress-softening. We took notice of polymer chains bridging fillers (Isono et al (1984), Klueppel.M (2003)) as in the our previous study, and measured the change of those to investigate the mechanism of polymer bond stress. A subset of short polymer paths connecting two adjacent fillers in the uniformity arranged model was measured as polymer bond stresses of both models were almost the same. 50 polymer chains in each filler pair were isolated, and Figure 8 illustrates the subset of short polymer paths consisting of 40 polymer bonds or less decreases versus the nominal strain. Furthermore, a representative change of the polymer path under cyclic deformation was visualized in Figure 9. In the 1st loading, the subset of short polymer paths decreases as strain increases. This decrease means an increase of long paths, and results from the change of filler positions during deformation. In other words, polymer paths connecting fillers become longer to ajust to the increase of filler-filler distance sliding on filler surfaces. During loading process, bonds of polymer paths are stretched, so that the polymer bond stress of the 1st loading become large. In the subsequent 1st unloading, extended long polymer paths fold as end beads of polymer paths are absorbed on filler surfaces without a change in polymer path length, even though filler-filler distance decreases. This change of polymer paths leads to the small

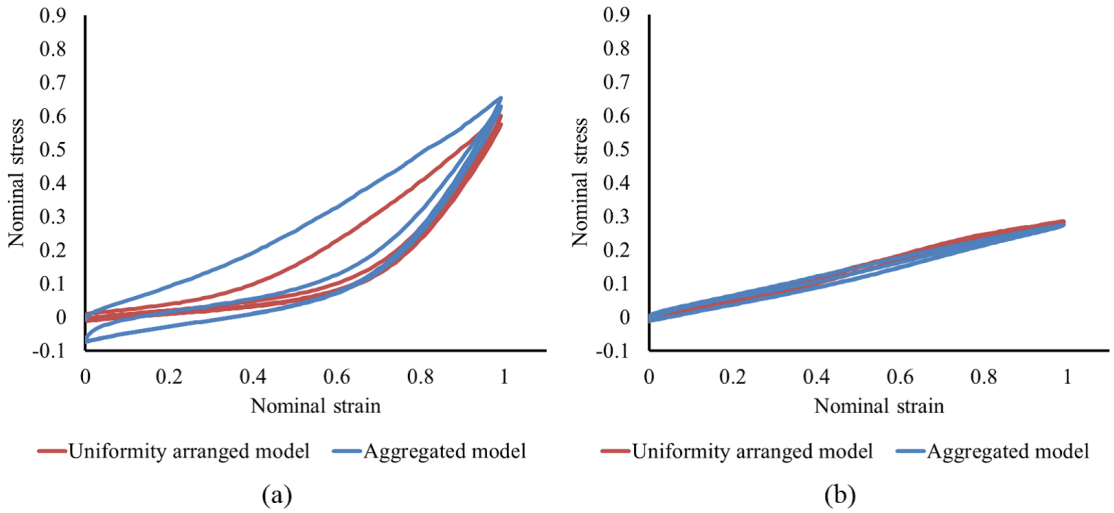


Figure 6: Decomposed stress-strain curves of the uniformity arranged model and the aggregated model:(a) bond stress; (b) nonbond stress.

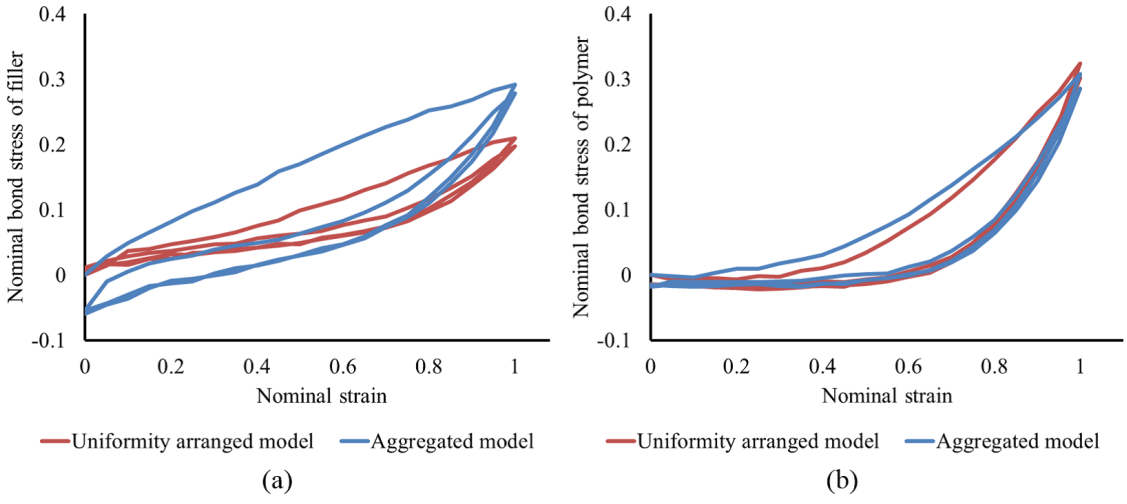


Figure 7: Decomposed bond stress-strain curves of the uniformity arranged model and the aggregated model:(a) filler phase; (b) polymer phase.

change of the subset of short polymer path during 1st unloading and loose/folded polymer chains between fillers at the end of 1st unloading. Hence, folded polymer paths are only unfolded during the 2nd loading despite the filler-filler distance increases. This phenomenon is attributed to small change of the subset in the 2nd loading, and stress does not increase compared to the 1st loading because bonds of polymer paths are not stretched. However, stress of the 2nd loading increases near the largest strain of the 1st loading as polymer paths become stretched state again.

The aforementioned change of polymer network induces hysteresis and stress-softening from polymer dynamics from the uniformity arranged model point of view. A similar change can be induced in the aggregated model as the polymer bond stress of the aggregated model is close to the uniformity aggregated model. In addition, the polymer conformation between filler aggregates may be changed during deformation in the aggregated model, even though polymer chains between adjacent filler particles in the deformation direction of the system mainly become longer in the uniformity arranged model. The study on the change of polymer network in the aggregated model is a future issue.

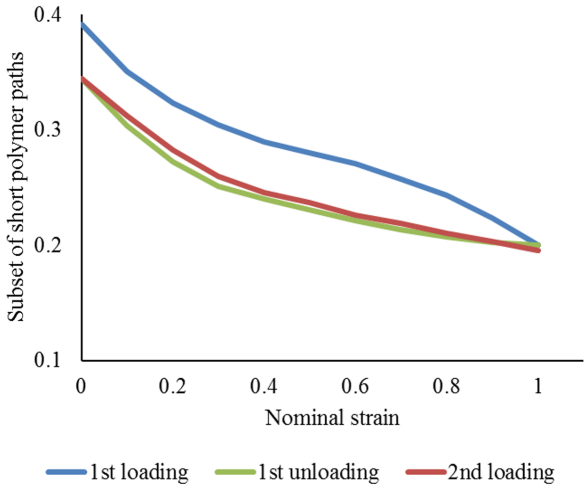


Figure 8: Subset of short polymer path in uniformity arranged model.

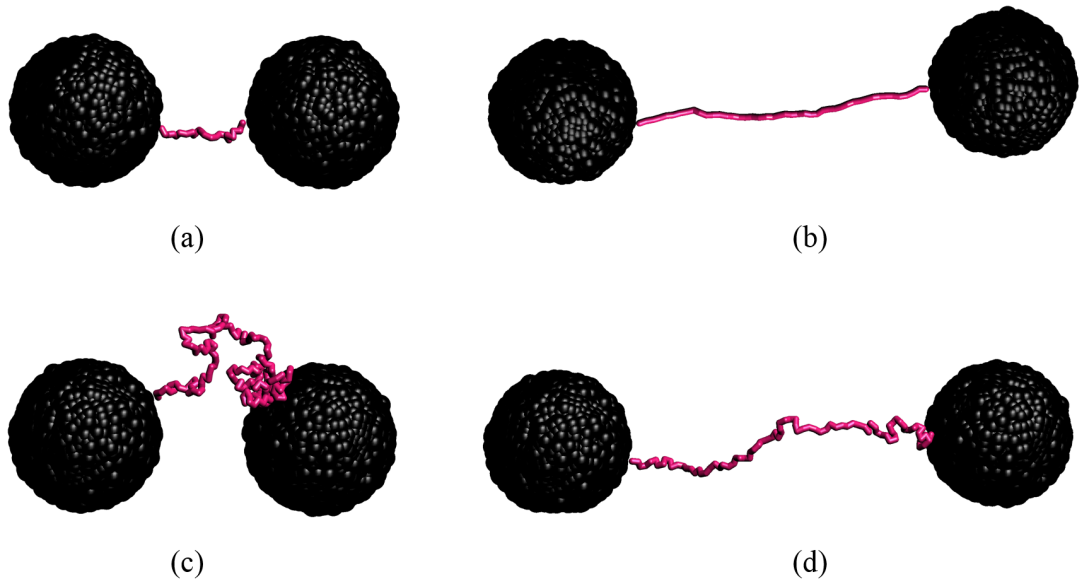


Figure 9: Conformational change of a polymer path bridging fillers;(a)at the initial state, (b)at the end of 1st loading (beginning of 1st unloading), (c)at the beginning of 2nd loading (end of 1st unloading), (d)at the end of 2nd loading. Black spheres and magenta lines represent filler particles and polymer chains, respectively.

6 Contribution of Filler to Mechanical Behavior

First, changes of filler positions during the two cycles were measured to investigate a relationship between filler morphology and filler deformation. Figure 10 presents mean-square distances (MSD) of filler positions from affinely deformed positions of fillers at the beginning of the 1st loading. We defined MSD as:

$$MSD = \frac{\sum_{i=1}^{N_{NP}} \left(\mathbf{r}_i\left(\epsilon\right) - \mathbf{a}_i\left(\epsilon_0\right)\right)^2}{N_{NP}} \tag{4}$$

where $N_{NP} = 1000$; the total number of filler particles, $\mathbf{r}_i$ is the position of center of a ith filler and $\mathbf{a}_i$ is the positions of affinely deformed position of the ith filler at ϵ_0. Zero in the vertical line denotes the complete affine deformation. The greater the value is, the greater the deviation from the affine deformation. We can see the uniformity arranged model deforms almost affinely during the two cycles represented in Figure 10 (a). On the other hand, the differences of the aggregated model become larger as the deformation proceed. It is supposed that collision or contact between fillers caused the difference, collision/contact disturb the change of filler position, unlike the uniformity arranged model. Figure 10 (b) illustrates that deviation from the affine deformation of the 2nd loading in the aggregated model is smaller than the 1st loading and less collision/contact occurs during the 2nd loading.

Filler bond stress components of both models for the stretching direction and the compression direction of the system were compared. The results, the differences of stress components obtained by subtracting the uniformity arranged model from the aggregated model, are presented in Figure 11. Values at strain 1.0 in the 1st loading, where the difference between models becomes the maximum, and values at strain 0.7 in 2nd loading, where the difference from 1st loading is almost maximum, in other words stress-softening effect is the almost greater, are presented.

In the 1st loading, both the Z components, which is parallel to the stretching direction of the system, and X/Y components, which is perpendicular to the stretching direction, are large, but the positive and negative values are opposite. This means the filler deformation in the aggregated model is larger than the uniformity arranged model: fillers extend in Z direction and are compressed in X/Y direction. This filler compression is due to collision of fillers. In loading, non-compression condition of the system leads both the compression of the system along the X/Y direction and decreases of filler-filler X/Y distance, and the collision of fillers are induced. As the deformation of the system proceeds, fillers are compressed in the X/Y direction and stretch in the Z direction. Consequently Z component of the filler bond stress and therefore the stress of the system grow.

On the other hand, filler deformation of the aggregated model in 1st unloading is the reverse of 1st loading. Fillers are compressed in the Z direction (unloading direction of the system) and strech in the X/Y direction. The change of the deformation direction of the system (Z $\rightarrow$ X/Y) induces a change of the filler-filler contact as follows. Z direction is compression direction of the unloading even though the system stretches along this direction in the loading, hence Z component of filler-filler distance decreases, and fillers can contact with other fillers in the Z direction. The stretch of fillers in the X/Y direction reduces the Z stress component of the system significantly; as a result the filler bond stress plunges.

As described above, it was found that fillers in the aggregated model deform more than the uniformity arranged model. This difference of filler deformation leads the increase of hysteresis of the 1st loading due to “the increase of filler bond stress in loading” and “the decrease in unloading”.

Figure 11 shows that the difference of the filler bond stress in the 2nd cycle is clearly lesser than the 1st cycle. In particular, the value of Z direction, stretching direction of the system, in the 2nd loading is almost zero. It is inferred that there are few differences in the filler deformation between both models. This implies that the reduction of the filler bond stress and thus the stress of the system during the 2nd loading is attributed to the decrease the difference in hysteresis of the 2nd cycle between both models. Moreover, not only the difference of the filler bond stress, but also the filler bond stress itself decrease during 1st loading as shown in Table1. This table tells us the filler bond stress of the 2nd cycle is lesser than the 1st loading, so the stress-softening is induced, and the hysteresis decreases.

Meanwhile the positive value in the upper right of Table 1 indicates that fillers of the uniformity arranged model in which fillers do not contact with another filler particle stretch in the Z direction. It is supposed that the interaction between filler and polymer deforms fillers. As described in Section 5, polymer paths bridging filler particles

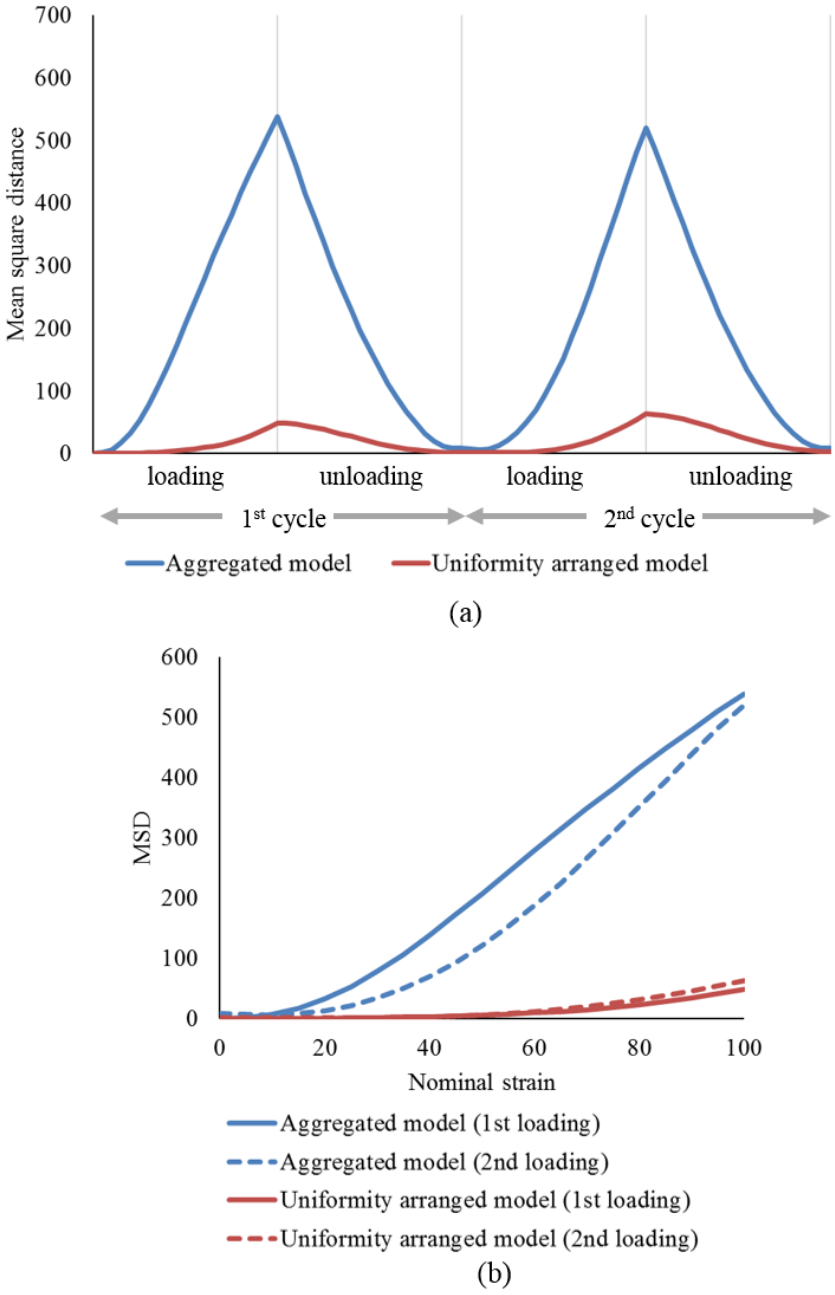


Figure 10: Mean square distance (MSD) of filler positions from affine deformation;(a) MSD versus time, (b) MSD versus strain.

Table 1: Stress Component in elongation direction of the system at strain 0.7.

	the aggregated model	the uniformity arranged model
1st loading	0.76	0.58
2nd loading	0.49	0.47

become longer along the stretching axis of the system sliding on the filler surface to adjust the increase of filler-filler distance particularly in the 1st loading. Therefore, polymer bonds constituting polymer paths are stretched, and polymer paths become called “extended-chains”. The entropy effect of chains, namely the force to return to the coil where the energy of chains is lower, extends fillers in the stretching axis of the system. In the subsequent 2nd loading, polymer chains between filler particles are loose at the beginning of the 2nd loading and are not stretched during the loading, so that both the force acting on fillers from polymer chains and filler deformation are smaller than the 1st loading. In short, the change of polymer conformation, the major source of polymer bond stress, is also the source of the filler bond stress (filler deformation). We can deny that there is not a relationship between the polymer bond stress and the filler bond stress.

The filler bond stress of the aggregated model is greater than the uniformity arranged model due to filler deformation caused by filler collision in addition to the interaction force with polymer.

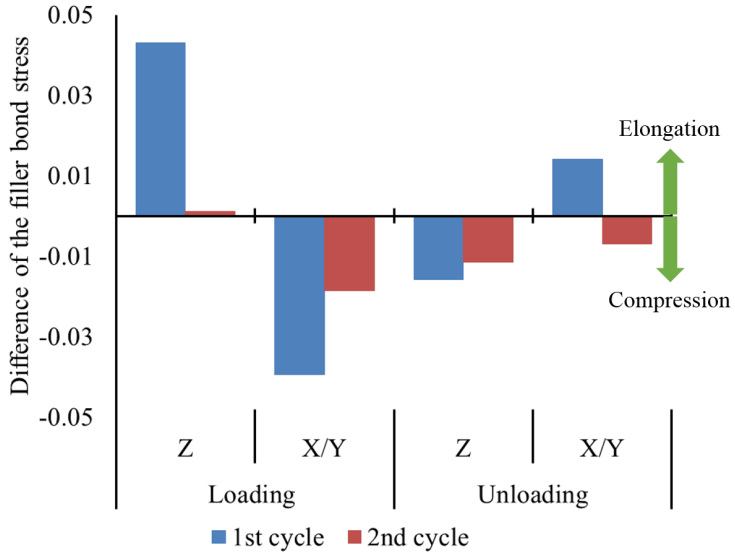


Figure 11: Difference of filler bond stress. The value obtained by subtracting the components of the uniformity arranged model from the aggregated model. Z direction is the stretching direction of the system and X/Y direction is the compression direction. Positive value means the extension of the filler and negative value means the compression of the filler.

The number of filler aggregates, contact force, and contact area between filler particles were measured in order to investigate a reason for the change of contact/collision between fillers (see Figure 12). Filler particles, between which the distance was less than 1.0, were considered as a filler aggregate, since filler particles were not physically bonded to each other. The contact area is the number of filler beads constituting filler particles and interacting with another filler particle. The contact force is the summation of the Lennard-Jones force between filler beads interacting with another filler particle. Figure 12(a) indicates there is no contact between fillers in the uniformity arranged model within the maximum strain of this study as the number of aggregate is equal to 1000–the total number of filler particles. For this reason, Figure 12(b) and (c) present only the results of the aggregated model. The number of the filler aggregates of the aggregated model increases particularly in the 1st loading. This means a breakage of the filler aggregates. As a result of the breakage, both the contact area and force decrease in the 1st loading. After the 1st loading, the contact force and area continue to decrease gradually, even though the change in the number of the filler aggregate is small. It is inferred that the decrease of aggregates results from the local change of filler aggregate, re-aggregate and breakage of filler particles. This decrease of contact force and area induces the decline of the filler bond stress and thus hysteresis, and stress-softening under cyclic deformation. In short, the decrease of contact force and area between filler particles caused by the breakage of filler aggregate induces the decrease of filler deformation or filler stress–the stress-softening and hysteresis.

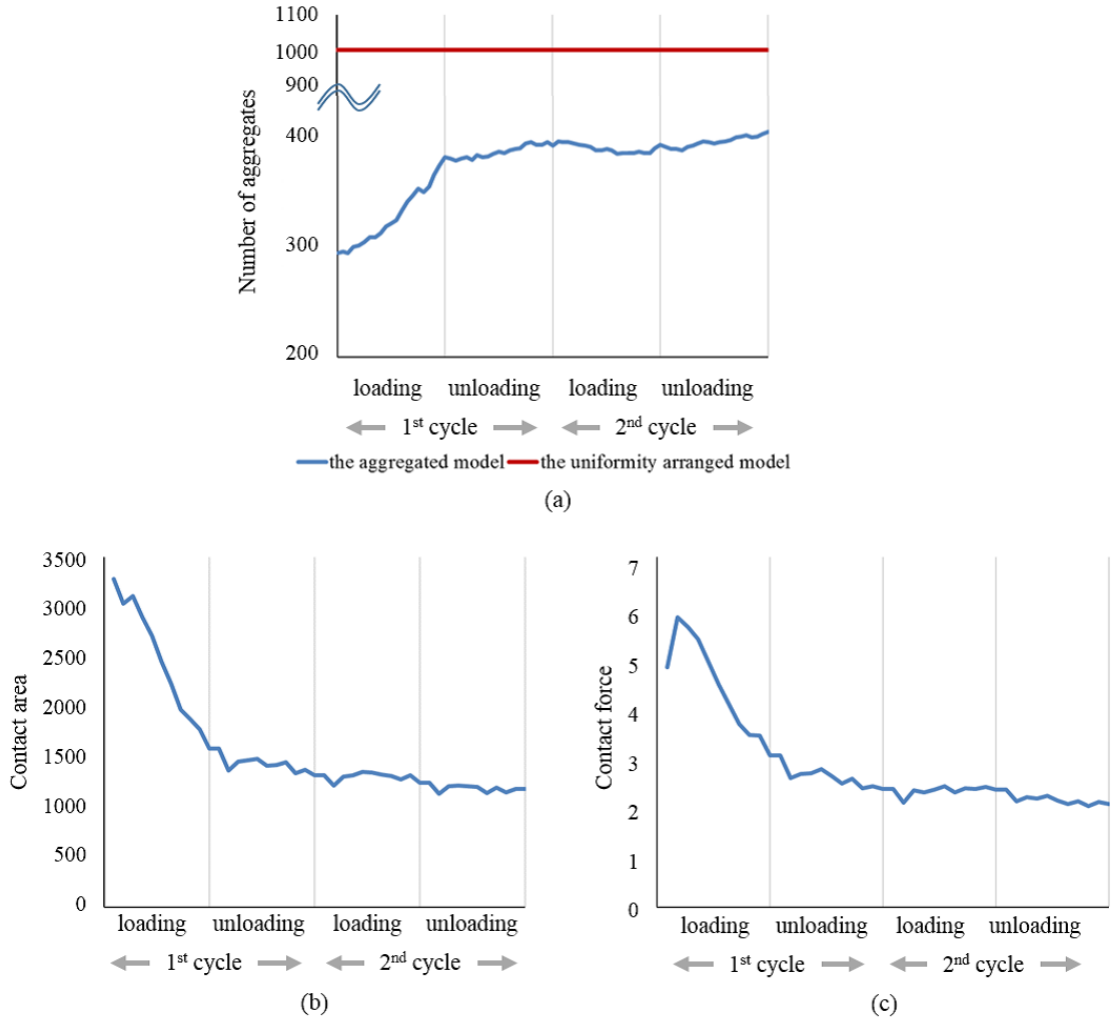


Figure 12: Contact information between fillers; (a)the number of aggregates, (b)contact area between fillers: the number of filler beads interacting with another filler particle, (c)contact force between fillers: summation of LJ force between filler beads caused by the contact with another filler particles. constituting another filler particle.

7 Conclusion

We succeeded in reproducing the characteristic behaviors, i.e. not only hysteresis, stress-softening, and permanent-set but effects of filler morphology of filled rubber under cyclic deformation, using large-scale coarse-grained molecular dynamics simulation. Analyzing the stress-strain curves, filler morphology, and polymer chain network, we determined the followings regarding the the mechanics of mechanical behavior of filled rubber:

- The difference in the mechanical behavior under cyclic deformation of systems with different filler morphology are due to mainly filler deformation.
- Both the contact between fillers and the interaction with polymer chains deform filler.
- In the aggregated model, in which the mean distance between fillers is shorter than the uniformity arranged model, fillers are easy to deform during deformation.
- Stress-softening which is attributed to filler is induced by a decrease of contact force and area between filler particles due to the breakage of filler aggregate in primary loading. As a result, hysteresis in the 2nd loading become less.
- The differences in filler contact between loading and unloading result in differences of filler deformation, and result in hysteresis.
- Hysteresis and stress-softening which are attributed to the polymer phase are caused by the conformational change of polymer chains between fillers during primary loading.

These results lead to the conclusion that not only the interaction between filler and polymer but the morphological change of filler are the sources of those characteristic behaviors. In this paper, the effect of filler type, such as carbon-black and silica, their interactions with polymer are different, radius of filler, and thickness of interphase are not studied. These are subjects for our future research.

We have shed some light on the mechanics of filled rubber. Considering knowledge obtained from this study, we accelerate the design of improved materials for high-performance tyres.

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