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Deformation behavior of silica-filled rubber with coupling agents under monotonic and cyclic straining

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ABSTRACT

A new constitutive equation for rubber is derived by employing a nonaffine molecular chain network model for elastic deformation behavior and the reptation theory for viscoelastic deformation behavior. The effect of a silica coupling agent, whose condensation reaction heterogeneously creates a crosslinking agent that increases the number of entangled points, on the deformation behavior is evaluated through the nonaffine constitutive equation for rubber. Precise TEM observation suggests the generation of complex interfillers connecting gel phases in which the characteristics of rubber intricately changed depending on the volume fraction of the silica coupling agent. The deformation behaviors of 2D rubber unit cells containing silica fillers under monotonic and cyclic strainings are investigated by computational simulation based on the proposed constitutive equation and the homogenization method. The obtained results clarified the essential physical enhancement mechanisms of deformation resistance and hysteresis loss, i.e., the Mullins effect, for silica-filled rubber. The volume fraction of the silica coupling agent essentially affects the deformation behavior of silica-filled rubber, the finding suggests that the material characteristics of silica-filled rubber are much more controllable than those of carbon-black-filled rubber.

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1. Introduction

It is well known that rubber exhibits a complex deformation behavior under monotonic and cyclic straining. Hysteresis loss, i.e., the Mullins effect [1,2] during cyclic loading processes, depends on the applied strain rate, which in turn is strongly related to the filling of particles such as carbon-black(CB) and silica. Therefore, very intensive researches have been conducted the modeling of unfilled rubber and CB-filled rubber. The manifestations of hysteresis and the viscoelastic response of unfilled rubber were explained by the change in the entanglement situation of the molecular structures [3], the slipping of the molecular chain [4], and the interaction of springs with the surroundings [5–7]. For CB-filled rubber, the mechanism for the manifestation of the characteristic response caused by the microscopic deformation behavior that depends on the volume fraction and distribution morphology of CB has been clarified in detail by the homogenization method using 2D and 3D unit cell models [3,8–11].

Thus far, we have developed a nonaffine model that accounts for the change in the entanglement situation of the molecular

network structure [12–14] and constructed a computational model for CB-filled rubber using the proposed constitutive equation and the homogenization method [15]. The strain-rate-independent mechanical characteristics of unfilled rubber and CB-filled rubber have been investigated [3], and the mechanism of the enhancement in the mechanical characteristics of rubber upon CB filling has been clarified. The elaborated 3D model enables us to clarify the effect of the distribution morphology on the deformation behavior of CB-filled rubber [10,11]. The obtained results have been extensively used to develop new materials for automobile tires [16,17].

Owing to the wide range of controllability of mechanical characteristics achieved by adding a coupling agent and the use of environment-friendly materials, silica-filled rubber has been drawing significant attention and finding extensive usage. In this study, to clarify the essential mechanism of the marked increase in the deformation resistance of silica-filled rubber, we will construct a finite element homogenization model for silica-filled rubber with a simple unit cell. This model can reflect newly clarified experimental observations that include the existence of heterogeneously distributed cross links in rubber filled with silica coupling agents [18] (the gel phase), and the bunching like gel structures developed from the interfacial phase between rubber and silica particles. As in the case of a heterogeneously distributed cross links in glassy polymer [19,20] the heterogeneous

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distribution of cross links may affect the micro- to macroscopic deformation behavior of silica-filled rubber. Nevertheless, we do not have sufficient information associated with the concrete distributions of cross links, therefore, in this investigation we will assume simple distributions of average number of segments (N) and clarify the effect of heterogeneity and distribution patterns on the micro- to macroscopic deformation behaviors of rubber. The computational prediction may suggest the capability of the present method to provide a tool for evaluating the effect of the addition of coupling agent on the fundamental deformation behavior of silica-filled-rubber.

2. Constitutive equation

2.1. Constitutive equation for homogeneous rubber

In order to reproduce the experimentally observed characteristic features of rubber, its microstructure is assumed to consist of long molecular chains randomly distributed in space. A single chain, which consists of several segments containing monomers, is defined by two linkages, that are assumed to be chemically or physically entangled points of molecular chains. The physical links are, in general, not permanent and may change depending on deformation. On the other hand, chemical links are generally permanent and preserve the entanglement situation. The decrease in the number of entangled points upon deformation increases the average number of segments N in a single chain, enhances extensibility, and reduces the stiffness of the material, i.e., softening. All these effects play very important roles in the manifestation of the hysteresis of the cyclic deformation behavior of strain-rate-independent rubber [3]. To account for the change in the number of entangled points, a nonaffine molecular chain network theory was developed [12–14]: according to this theory, the number of entangled points is expressed as a suitable function of temperature and an appropriately defined measure of deformation.

The long molecular chains are in contact with other chains at many points, which is the potential source of the viscoelastic response. Therefore, a chain easily moves along the chain direction; however, its movement with respect to its normal direction is restricted. A tube can represent this type of restriction, upon the application of deformation. The molecular chain relaxes with respect to the chain and normal directions in a short time, and subsequently, it moves along the chain direction with long-term relaxation. This is the reptation theory that can easily account for the interaction between chains and their surroundings [5–7].
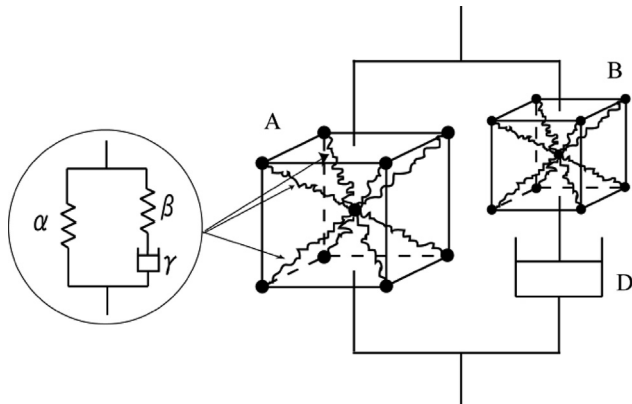

Fig. 1. Constitutive model consists of a revised eight-chain model A [11] containing standard elements; α and β are Langevin springs and γ is a dashpot, standard eight chain model B [21] and dashpot D.
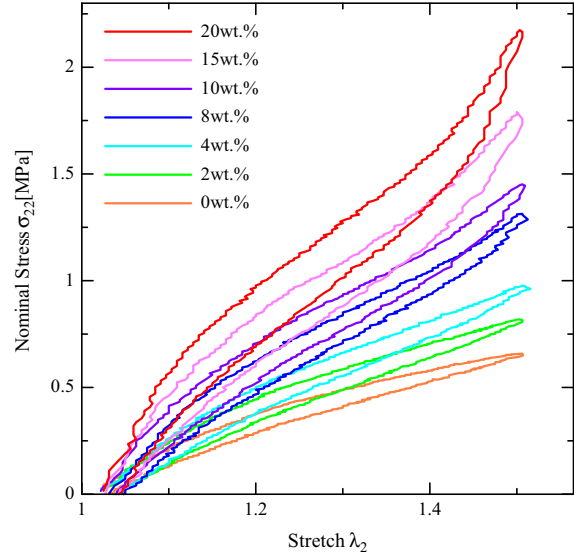

Fig. 2. Nominal stress–stretch relations for silica-filled rubber with different weight percents of silica coupling agent [22].

The most typical characteristic of the present eight-chain model is that it contains eight standard models, as depicted in Fig. 1. This is because the viscoelastic response of rubber arises from the interaction of chains with their surroundings; therefore, the component chains of the eight-chain model should exhibit a viscoelastic response. The two springs α and β represent single Langevin chains, and dashpot γ represents the viscoelastic nature of rubber, which is modeled using the reptation theory [5–7].

Here $C_\alpha^R = n_\alpha k_B T$, $C_\beta^R = n_\beta k_B T$, $C_B^R = n_B k_B T$, and $n = n_\alpha + n_\beta + n_B$; n is the number of chains in the unit volume, k_B is Boltzmann's constant. N_α, N_β and N_B are the average numbers of segments for the springs α, β and B, respectively, and $\sqrt{N_\alpha}$, $\sqrt{N_\beta}$ and $\sqrt{N_B}$ are the corresponding limiting stretches. λ_α, λ_β and λ_γ are the stretches of the springs α, β and the dashpot γ, respectively, and $\lambda_c = \lambda_\beta \lambda_\gamma$. λ_{cB} and λ_D are the stretches for the eight-chain model and dashpot, respectively. Using the Langevin function L, we derived the relationships between the principal deviatoric stresses σ'_{Ai} and stretches λ_i as follows:

$$\sigma'_{Ai} = \frac{1}{3}\left\{ C_\alpha^R \sqrt{N_\alpha} L^{-1}\left(\frac{\lambda_c}{\sqrt{N_\alpha}}\right) + C_\beta^R \sqrt{N_\beta}\frac{1}{\lambda_\gamma} L^{-1}\left(\frac{\lambda_\beta}{\sqrt{N_\beta}}\right)\right\}\frac{\lambda_i^2}{\lambda_c} \qquad (1)$$

For the eight-chain model B shown in Fig. 1, we derived the relationships between the principal deviatoric stresses σ'_{Bi} and the stretch λ'_i becomes [21]

$$\sigma'_{Bi} = \frac{1}{3}\left\{ C_B^R \sqrt{N_B} L^{-1}\left(\frac{\lambda_{cB}}{\sqrt{N_B}}\right)\right\}\frac{\lambda_i'^2}{\lambda_{cB}} \qquad (2)$$

For dashpots γ and D, the viscoelastic shear strain rates $\dot{\gamma}^\gamma$ and $\dot{\gamma}^D$ are indicated as [7,11]

$$\dot{\gamma}^\gamma = C_1^\gamma(\lambda_\gamma - 1)^{C_2^\gamma}\tau_\gamma^{*m_\gamma}$$

$$\dot{\gamma}^D = C_1^D(\lambda_D - 1)^{C_2^D}\tau_D^{*m_D} \qquad (3)$$

where τ_γ^*, τ_D^* are respectively representative shear stress defined by driving stresses σ^γ and σ^D for the viscoelastic strain rate $\dot{\gamma}^\gamma$ and $\dot{\gamma}^D$. C_1^γ, C_2^γ, m_γ, C_1^D, C_2^D and m_D are material parameters representing strain rate sensitivity of materials.

By adding a coupling agent, the mechanical characteristics of silica-filled rubber are markedly changed. Fig. 2 indicates the nominal stress–stretch relationships for silica-filled rubber with