XXI ICTAM, 15–21 August 2004, Warsaw, Poland

COMPUTATIONAL CHARACTERIZATION OF MICRO- TO MACROSCOPIC MECHANICAL BEHAVIOR OF CARBON BLACK-FILLED RUBBER

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INTRODUCTION

It is well known that the blending of particulate fillers such as carbon black induce an increase in ultimate properties such as tear and tensile strength and abrasion resistance [1]. Fillers also increase the moludus of elasticity. The hysteresis loss, i.e., Mullins effect [2], during loading and unloading processes for carbon black-filled rubber is marked as compared with that of unfilled rubber, which is strongly related to the ultimate properties of filled rubber [2]. Here, we focus our attention on the computational evaluation of the enhancement of deformation resistance and hysteresis loss, caused by filling carbon black to rubber.

The constitutive equation for rubber is established by employing a nonaffine molecular-chain network model [3], which may account for the change of the entanglement situation during the deformation processes. Meanwhile, the carbon black is assumed to be sufficiently hard compared with rubber and the deformation behavior is governed by the linear elastic constitutive equation. The computational simulations employing these constitutive equations and unit cell models of rubber containing carbon black clarify the mechanisms of enhancement of deformation resistance and hysteresis loss, and the effect of volume fraction and distribution patterns of carbon black on these characteristics. The computationally predicted results and experimental results are compared to evaluate the adequacy of the present simulation.

CONSTITUTIVE EQUATION AND COMPUTATIONAL MODEL

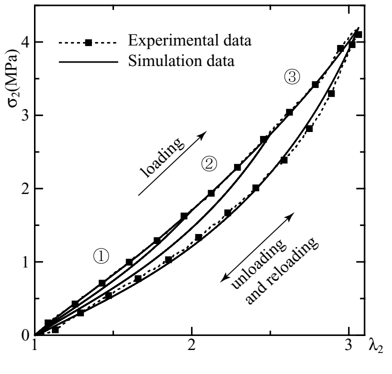

Figure 1. Hysteresis of unfilled rubber under cyclic loading.

It has been suggested that a network is formed by linking polymer chains together, and this linkage may be either physical or chemical. The physical links are, in general, not permanent and may change depending on deformation and temperature change. On the other hand, chemical links are permanent and preserve the entangled situation. The physical links play a very important role in the manifestation of the hysteresis of cyclic deformation behavior of rubber [4]. The decrease in the number of entangled points due to deformation causes the increase of the average number of segments in a single chain, enhanced extensibility, and the reduction of the stiffness of the material, i.e., softening. Here, we employ the nonaffine molecular-chain network model [3] to accommodate the change in the average number of segments N depending on stretch λ_c, as $N(\lambda_c) = N_0 + f(\lambda_c)$, where N_0 is the initial average number of segments in a single chain, $f(\lambda_c)$ is a polynomial which suitably expresses the experimental results, and we employ the quartic expression of λ_c.

Figure 1 indicates the true stress-stretch relationship for unfilled rubber under cyclic loading. The dotted lines represent the experimental results. To reproduce the experimental results, we identify the concrete form of $N(\lambda_c)$, by the least mean squares method, for the loading process of the first cycle and it is preserved during the unloading process. Furthermore, the number of segments N is preserved until stretch λ_c due to subsequent loading reaches the maximum value of previous loading processes. The corresponding stress-stretch relationships shown in Fig.1 by solid lines approximately reproduce the experimentally obtained results.

The mechanical characteristics of carbon black-filled rubber are strongly dependent on the volume fraction and distribution patterns of carbon black. Although the distribution of carbon black is somewhat random to aggregated, here, we assume that it is periodic and evaluate the detailed characteristics of microscopic deformation and clarify their effect on the macroscopic mechanical characteristics of carbon black-filled rubber. The discussions are focused on the essential feature of the effect of volume fraction and distribution patterns on the mechanical characteristics of carbon black-filled rubber.

Figure 2 shows the computational model in which heterogeneous carbon black is assumed to be distributed periodically. As indicated in Fig.2, in the present investigation, the heterogeneous carbon black is assumed to comprise circular cylinders of radii of curvature r_1 and r_2 contained in a square unit cell. Case A corresponds to carbon black distributed throughout the unit cell, and Case B is the somewhat aggregated case. The homogenization method [5] has been employed to correlate the micro- to macroscopic deformation behavior.

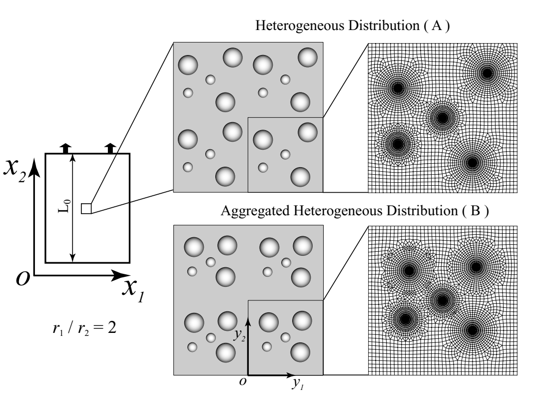

Figure 2. Simulation models of carbon black-filled rubber with volume fraction 20%.

For a typical unit cell, which is the microscopic element of carbon black-filled rubber, a macroscopically homogeneous strain is applied. The material parameters for the rubber employed are $N_0 = 4.5$, $N_a = 4.36 \times 10^{26}$, $C_0^R = n_0 k_B T =$

0.394, $n_0 = N_a/N_0$, and $T = 296K$ [6]. For carbon black, elasticity modulus and Poisson's ratio are $E_c = 100\text{MPa}$ and $\nu_c = 0.3$ respectively. To suppress the onset of numerical instability caused by the extreme difference between the stiffnesses of carbon black and rubber, rather low stiffness for carbon black is introduced. It has, however, been verified that this value provides suitable results.

RESULTS AND DISCUSSION

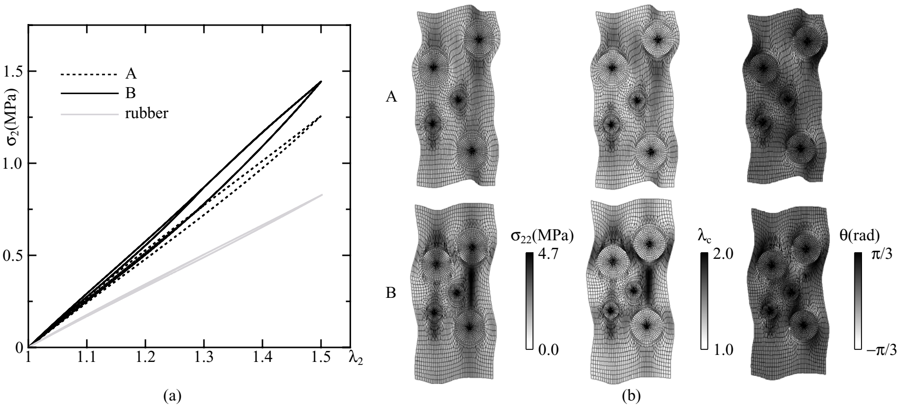

Figure 3. Deformation behavior of carbon black-filled rubber with $f_0 = 20\%$. (a) True stress-stretch relationships. (b) Distribution of stress, stretch and rotation for cases A and B at deformation stage $\lambda_2 = 1.5$.

Three cyclic deformations up to maximum average stretches of 1.1, 1.3 and 1.5 for 1st, 2nd and 3rd cycles, respectively, are simulated. Figure 3(a) shows the typical true stress-stretch relationships for unfilled rubber and carbon black-filled rubber for cases A and B in Fig.2. Carbon black-filled rubber exhibits markedly high deformation resistance as compared with unfilled rubber. The aggregated distribution of carbon black, case B, contributes to the further increase of deformation resistance. The resistance to deformation rises with an increase of the volume fraction of carbon black f_0.

As indicated in Fig.3(b), the concentrated deformation connecting the carbon black causes high stretching accompanied by locally large rotation in the surrounding area of highstretch. The orientation hardening of rubber develops in the highly stretched area where the resistance to deformation rises and the stress attains a high value. On the other hand, in the highly rotated area, deformation is mainly absorbed by rotation and orientation hardening is suppressed, which limits the stress to a rather low value. The localized deformation connecting large particles is much stronger, therefore, in addition to the distance between the particles, heterogeneity of the particles also affects the deformation resistance. The increase of the volume fraction of carbon black reduces the particle spacing, which facilitates the emergence of localized deformation connecting the particles and high resistance to deformation. Thus an additional increase in deformation resistance is expected upon filling the rubber with carbon black.

Furthermore, as indicated above, the higher concentration of the deformation causes locally high stretch in rubber, which promotes the change of the average number of segments. As a result, this contributes to the manifestation of hysteresis loss, i.e., Mullins effect, in the cyclic stress-stretch relationships.Figure 4 indicates the hysteresis loss for 1st, 2nd and 3rd cycles for unfilled rubber and carbon black-filled rubber with patterns A and B. The hysteresis loss $\Delta\phi$ is defined by the difference in the areas under the stress-stretch curves for a loading cycle followed by an unloading cycle. Hysteresis loss $\Delta\phi$ increases with the increases of average stretch and aggregation of carbon black. Furthermore, the effect of the volume fraction of carbon black on hysteresis loss is substantial and is amplified with the increase in the number of cycles, in other words, the increase in the amount of stretch in the present loading processes. These are attributable to the softening caused by the change in the average number of segments due to the increase in the amount of stretch.

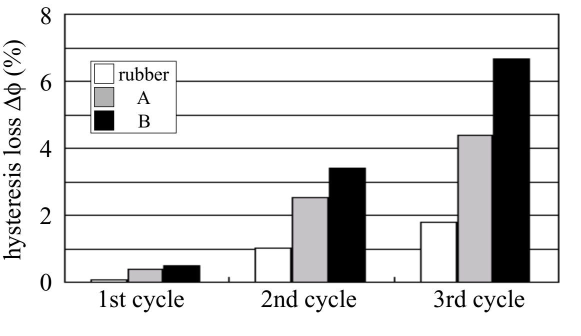

Figure 4. Hysteresis loss for different distribution patterns.

The results obtained partially clarified the essential physical enhancement mechanisms of deformation resistance and hysteresis loss, i.e., Mullins effect, for rubber filled with carbon black with different distribution patterns and volume fractions.

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