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Micromechanical Mechanism of Reinforcement and Losses in Filled Rubbers

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Filled rubbers, composed of elastomer matrixes reinforced by agglomerating nanosized carbon black or silica particles, are widely used in various applications including automotive tires and vibration mounts.[1,2] It is accepted that the striking reinforcement effects observed in filled rubbers can be attributed to the formation and breakdown of physical (van der Waals) bonds between the networking filler particles.[3−5] However, this mechanism is known to be by far insufficient to account for the markedly enhanced energy dissipation, so additional assumptions such as slippage of chain entanglements or partial release of elastically dead rubber trapped within filler agglomerates are commonly invoked to explain the losses.[4,5] This inconsistency is intriguing and somewhat surprising, as the stiffness and the losses constitute the real and imaginary parts of one and the same complex dynamic shear modulus.

Carbon blacks are by far the most widespread fillers used for industrial rubber products.[1,2] Carbon blacks consist of tiny nanoparticles fused into primary aggregates of around 50−100 nm in size with highly energetic, strongly adhering surfaces. In a rubber matrix, the primary aggregates tend to further agglomerate to form fractal clusters and, eventually, percolating networks at larger filler loadings.[4,5,10−12] Upon cyclic deformations, filled rubbers exhibit peculiar amplitude and frequency dependent nonlinear viscoelastic properties, often referred to as the Payne effect[3] (for a recent review and references, see ref 4). The dynamics of polymer segments is significantly hindered in the vicinity of filler surfaces, leading to the formation of a coating layer of immobilized glassy polymer.[4−9] The layer thickness Δ was estimated based on the scaling analysis of the effect of filler size on the stiffness of filled rubbers.[4] The results suggested $\Delta \approx 2$ nm, which agreed well with the estimates obtained by NMR measurements[7] and also with the values arising in the temperature−frequency superposition law.[8,9] In this Communication, we use the finite element method and show that the relationship between reinforcement and losses observed in filled rubbers can be explained micromechanically by taking into account that the networking filler particles are joined by coating layers of immobilized rubber and realizing that both storage and dissipation energies are strongly localized in these coating layers.

We study a model system composed of a rubber matrix reinforced by a percolating diamond network of nonoverlapping, almost touching identical spheres joined by coating layers of immobilized glassy polymer, see the sketch in Figure 1. Clearly, such an idealized model tends to overemphasize the networking character of carbon black reinforcing structures in filled rubbers and thus overestimate the density of the reinforcing adhesive joints. However, the model permits accurate micromechanical analysis of the characteristics of the adhesive joints, thus allowing one to elucidate the relationship between the storage $\mu'_{\text{eff}} = \text{Re}\ \mu_{\text{eff}}$ and loss $\mu''_{\text{eff}} = \text{Im}\ \mu_{\text{eff}}$ components of the effective complex dynamic shear modulus μ_{eff}, in particular in the limiting case of low strains where the measured μ_{eff} becomes amplitude independent.[4]

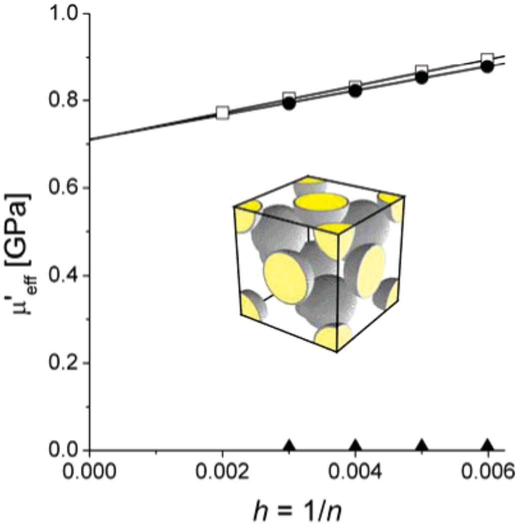

Figure 1. Asymptotic finite element predictions. Calculations were carried out on $n \times n \times n$ regular grids. Theoretically, for sufficiently large n, the estimates should converge asymptotically,[14,19] as indicated by the straight lines. Solid triangles give predictions for a two-phase composite consisting of a rubber matrix reinforced by silica spheres. Solid circles show results obtained with coated spheres, assuming a coating layer of glassy polymer of thickness $\Delta/R = 0.08$, where R is the sphere radius. Open squares stand for a corresponding two-phase composite without the rubber matrix, i.e., for a cellular microstructure system consisting of silica spheres joined by the coating layer of immobilized polymer. The sketch illustrates the geometric arrangement of the latter system (based on a grid of $n = 200$), with silica spheres shown in yellow and coating layers in gray.

The standard, displacement-based formulation of elasticity problems fails when Poisson's ratio approaches 0.5 and the material becomes incompressible. The use of mixed formulation avoids the difficulty.[14] Following on from our recent work,[15−19] we have developed a novel periodic mixed formulation solver for multiphase materials with nearly incompressible phases. We use serendipity family cubic shape brick elements with an incomplete cubic interpolation for the displacements and an element-based discontinuous interpolation for the pressure. Such elements are known to behave robustly in many related structural and fluid mechanics applications.[14] The resulting sparse matrix saddle point optimization problem was solved with a conjugate residual solver.[20] We have assumed typical material parameters for the constitutive phases. For the rubber matrix, we took a shear modulus of $\mu' = 10^{-3}$ GPa, Poisson's ratio $\nu = 0.4995$, and loss factor $\tan\delta = 0.1$, for the silica spheres, $\mu' = 30$ GPa, $\nu = 0.2$, and $\tan\delta = 10^{-6}$, and for the coating layer of immobilized polymer, $\mu' = 1$ GPa, $\nu = 0.35$, and $\tan\delta = 0.1$. We have studied periodic unit cells composed of 8 silica spheres separated by 1/100 of the unit cell edge, with a resulting sphere volume fraction of about 0.32, see the sketch in Figure 1. For the energy dissipation, we assumed a shear-dominated mechanism and estimated the effective loss modulus μ''_{eff} by equating the overall energy loss to the sum of the local losses, i.e., based on the relation $\mu''_{\text{eff}} = \langle \gamma^2(\mathbf{r})\mu''(\mathbf{r})\rangle$, where the angular brackets stand for the volume averaging, $\mathbf{r}$ is the radius-vector, $\mu''(\mathbf{r})$ is the local position-dependent loss modulus, and $\gamma(\mathbf{r})$ the amplification factor of the second-order invariant of the

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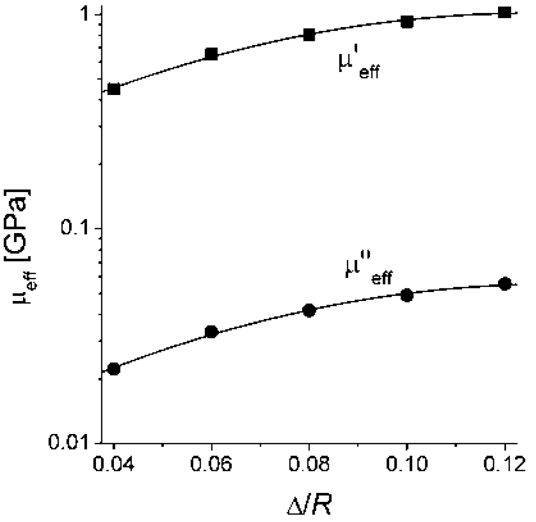

Figure 2. Numerical estimates for the effective storage and loss moduli. In the limiting case of low strain studied, the imposed deformations are vanishingly small and they do not affect the reinforcing filler network. In this context, the micromechanical mechanism controls the low-strain elastic reinforcement, whereas the degradation of the filler network brings about the softening effects at the strain amplitudes exceeding the yield point. Correspondingly, the micromechanical mechanism determines the losses at low strains, whereas the rearrangements of the filler network bring about loss variations at the larger strain amplitudes. For comparison, the unfilled rubber has $\mu' = 10^{-3}$ GPa and $\mu'' = 10^{-4}$ GPa.

deviatoric strain tensor. The latter was evaluated based on the displacement fields resulting from the finite element solutions.[21]

In Figure 1, filled triangles show predictions obtained in the absence of coating layers of immobilized polymer, i.e., for a two-phase composite composed of a rubber matrix reinforced by a regular diamond array of rigid silica spheres. The reinforcement is small, about a factor of 4 or so, corresponding well to the hydrodynamic-limit predictions of the classical three-sphere model,[13] but being by far too low to be representative of the stiffening effects observed in filled rubbers.[4,5] Upon introduction of a thin coating layer of a glassy polymer, one observes a pronounced reinforcement effect, see filled circles in Figure 1. To understand the role of the rubber matrix, we repeat calculations without the rubber matrix. The results are shown by open squares, and they indicate that the rubber matrix merely acts as a dispersing medium without any visual contribution to the effective stiffness. This behavior is in fact typical of real filled rubbers.[4]

Figure 2 presents results as a function of the coating layer thickness Δ, for the storage $\mu'_{\mathrm{eff}} = \mathrm{Re}\ \mu_{\mathrm{eff}}$ and loss $\mu''_{\mathrm{eff}} = \mathrm{Im}\ \mu_{\mathrm{eff}}$ components of the complex dynamic shear modulus μ_{eff}. One can see that both storage and loss moduli are strikingly enhanced compared to the unfilled rubber. However, the ratio $\tan \delta = \mu''_{\mathrm{eff}}/\mu'_{\mathrm{eff}}$ is practically independent of Δ, and it remains close to the $\tan \delta$ value of 0.1 assumed for the coating layer of immobilized glassy polymer. Such $\tan \delta$ loss factors are actually commonly observed in filled rubbers,[4] leading us to surmise that it is the coating layers of immobilized polymer which should determine the energy dissipation. Figure 3 supports this premise by revealing that the energy dissipation is indeed very much localized in the coating layers. Arrestingly, for a layer of thickness $\Delta/R = 0.04$ with R standing for the sphere radius, 99% of the energy dissipation is localized in ca. 0.1% of the system volume, inside the coating layer sections situated in the vicinity of the contact zones separating adjacent spheres. For comparison, for a typical carbon black filled rubber, $R \approx 50$ nm while $\Delta \approx 2$ nm, thus resulting in $\Delta/R \approx 0.04$.

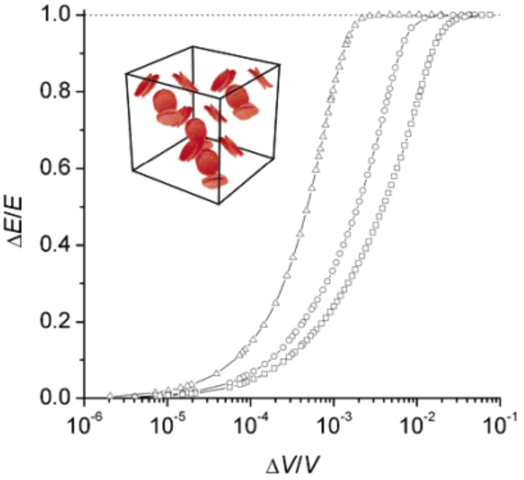

Figure 3. Localization of the energy dissipation. Open squares show results obtained assuming squares $\Delta/R = 0.12$, circles $\Delta/R = 0.08$, and triangles $\Delta/R = 0.04$. The grid elements were first sorted into ascending order according to their contribution to the energy dissipation and the cumulative distribution was then evaluated for the relative element volume fraction $\Delta V/V$ dissipating a given fraction $\Delta E/E$ of the total dissipation energy E. In the sketch, we show elements dissipating 99% of the total dissipation energy (based on a grid of $n = 200$, compare with the sketch in Figure 1). Similar localization behavior was observed for the storage energy.

The Payne effect does not depend on the polymeric nature of the matrix medium, and it is observed in a variety of filled systems including elastomer matrixes filled with carbon black and silica particles, cellulose whiskers and polymeric microgels, mixtures of carbon black with liquid decane or paraffin and clay/water systems.[4] This universality lends further support to the micromechanical mechanism of the reinforcement and energy dissipation, where the essential physics is described at a coarse-grained, mesoscopic level, whereas system-specific molecular level details are incorporated in the parameters of the mesoscopic level description.

Our results indicate that a simple micromechanical mechanism can explain the observed relationship between the reinforcement and the energy dissipation in filled rubbers. We have observed a remarkable localization of both storage and dissipation energy, found to occur primarily in the coating layers of immobilized polymer. These findings put a new emphasis on the role of the interfacial phenomena and suggest that the physical (van der Waals) forces responsible for the filler network formation may not necessarily directly affect the reinforcement and the losses but rather indirectly, by way of adhesive joints formed from the coating layers of immobilized polymer.

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