Supplementary Information

Novel Features of the Mullins Effect in Filled Elastomers Revealed by Stretching Measurements in Various Geometries

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Evaluation of real elongation in stretching process

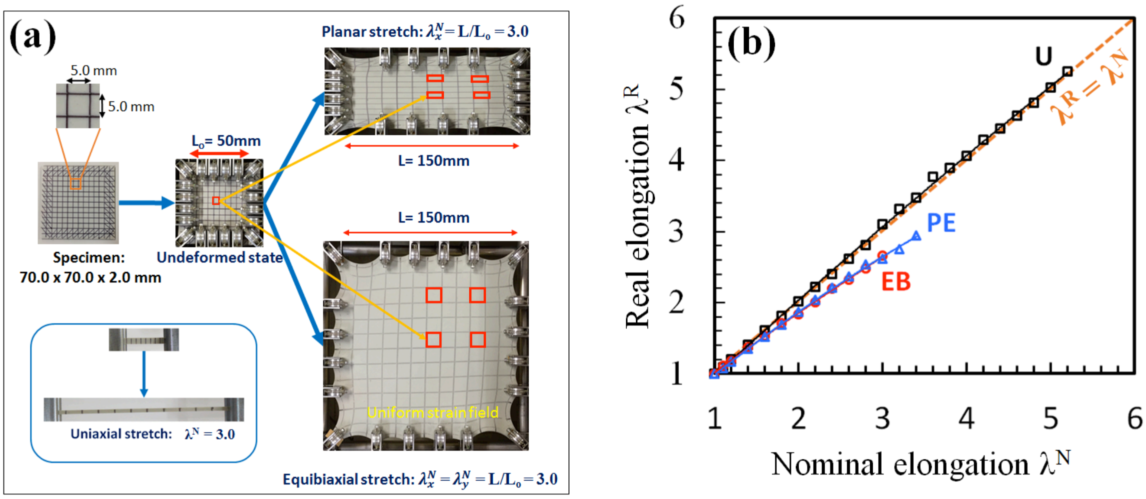

Fig. S1. (a) Photographs of the specimens with grids marked with 5.0 × 5.0 mm meshes in the undeformed state, and the states of planar and equibiaxial extension. (b) The relation of nominal elongation (λ^N) evaluated from the distance between the clamps and real elongation (λ^R) evaluated from the dimensional changes of the marked grids for equibiaxial (EB), planar (PE), and uniaxial (U) extension.

The grids marked with 5.0 × 5.0 mm meshes were sketched on the surface of the sheet specimens (70 × 70 × 2.0 mm) (Fig. S1a). The real elongation (λ^R) at the imposed deformation was evaluated from the dimensional changes of the marked grids. The value of λ^R at each deformation was obtained from the average of the values for several meshes. The stretching processes were recorded using a video camera, and the dimensional changes of the grids were measured using the Image J program 1.50i (National Institute of Health, USA.). The difference in local strain between different local sections was less than 3%, which confirms the uniformity of the imposed strain field. A similar method was applied for uniaxial deformation (Fig. S1a) of the rectangular specimens (65 × 6.0 × 2.0 mm). Figure S1b illustrates the relations between λ^R and nominal elongation (λ^N), which is evaluated from the distance between the clamps, for each deformation. The real elongation, λ^R, tends to be smaller than λ^N in biaxial extension, while no appreciable difference between λ^R and λ^N is observed in uniaxial extension. The relation between λ^R and λ^N is common to planar and equibiaxial extension, and it is well approximated by the following equation:

$$\lambda^R = 0.8288\lambda^N + 0.1712 \qquad (\lambda^N < 4) \tag{S1}$$

The real elongation λ^R is employed in the analysis of stress-strain data, i.e., $\lambda \equiv \lambda^R$.

The effective cross-section regarding the detected load in biaxial extension is estimated by comparing the values of the initial (small strain) modulus in uniaxial, planar, and equibiaxial extension (each of which is denoted as A_U, A_{PE}, and A_{EB}, respectively) on the basis of the linear elasticity theory.[1] As the present specimens are assumed incompressible with good approximation,[2] the relation is given by A_U:A_{PE}:A_{EB} =3:4:6. The effective cross-section for biaxial extension is determined from this ratio using the value of A_U obtained in uniaxial extension with a definite value of cross-section.

The sufficient magnitude of gauge length ($L_0 \approx 50$ mm), which is given by the distance between the clamps, effectively minimizes the effect of the inhomogeneous strain field in the vicinity of the clamps, because the area of the inhomogeneous strain field becomes negligibly small relative to that of the uniform strain field.

Effect of filler content (ϕ) on residual strain

Figure S2 displays the effect of filler content (ϕ) on the residual strain in reloading ε_r^r in uniaxial (U), equibiaxial (EB), and planar (PE) extension with λ_m=1.46 and 2.90. Residual strain ε_r^r slightly increases with an increase in ϕ in each extension with λ_m=1.46 and 2.90, although the values of ε_r^r are small, i.e., less than 0.1. When compared at the same ϕ, ε_r^r increases in the order of EB, PE and U.

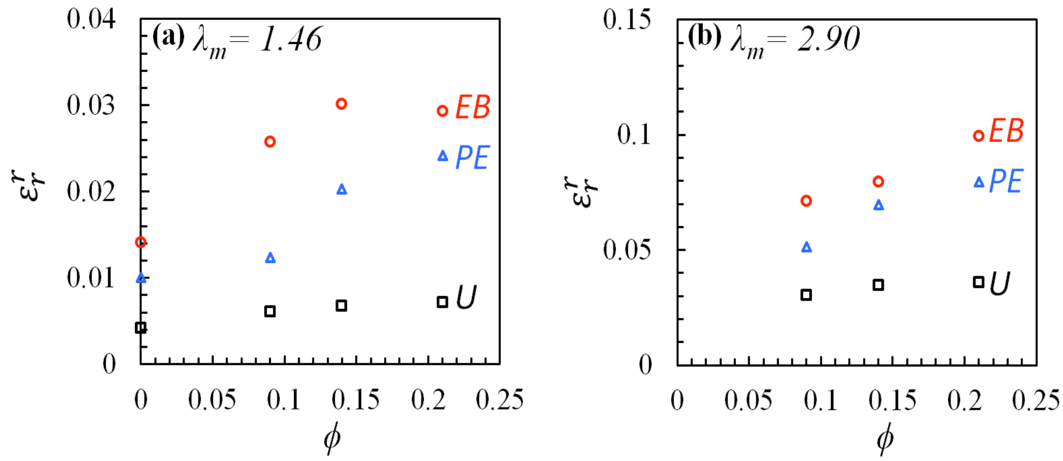

Fig.S2. Residual strain in reloading, ε_r^r, as a function of ϕ (volume fraction of filler) at λ_m=1.46 (a) and 2.90 (b) in uniaxial (U), equibiaxial (EB) and planar (PE) extension.

Effect of Silane-coupling agent (SCA) on residual strain and energy dissipation

Figure S3 shows the residual strains, ε_u^r and ε_r^r, for each type of extension as a function of λ_m for the specimen without SCA (ϕ = 0.21). Similarly to the specimen with SCA (ϕ = 0.21) , ε_r^r is smaller than ε_u^r when compared at the same λ_m, because a finite degree of strain recovery occurs as a result of the recovery or rearrangement of the filler-network structure during the equilibration time (30 min) after complete unloading.[3,4] Both ε_u^r and ε_r^r increase with an increase in λ_m for each type of extension. Residual strains are insensitive to type of deformation.

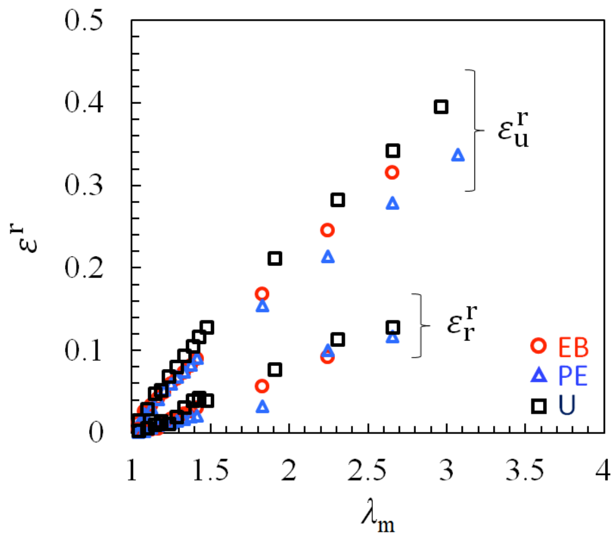

Fig. S3. The residual strains, ε_u^r and ε_r^r, in the stretching direction, evaluated from unloading and reloading processes, respectively, as a function of λ_m in uniaxial (U), planar (PE), or equibiaxial (EB) extension for SBR/silica without SCA of ϕ = 0.21.

Figures S4a and S4b illustrate D_u and D_r, respectively, as a function of λ_m for each type of extension for the specimen of ϕ = 0.21 with and without SCA. The results show that D_u is larger than D_r at the same λ_m, which is primarily because the stress in reloading is larger than that in unloading at the same λ due to the relation of $\varepsilon_u^r > \varepsilon_r^r$. Both D_u and D_r increase with an increase in λ_m for all types of deformation. Furthermore, both D_u and D_r are sensitive to the type of deformation: When compared at the same λ_m, EB shows the highest values, followed by PE, with U having the lowest. In general, both D_u and D_r of the specimen without SCA are quite larger than the specimen without SCA, especially in the small in formation.

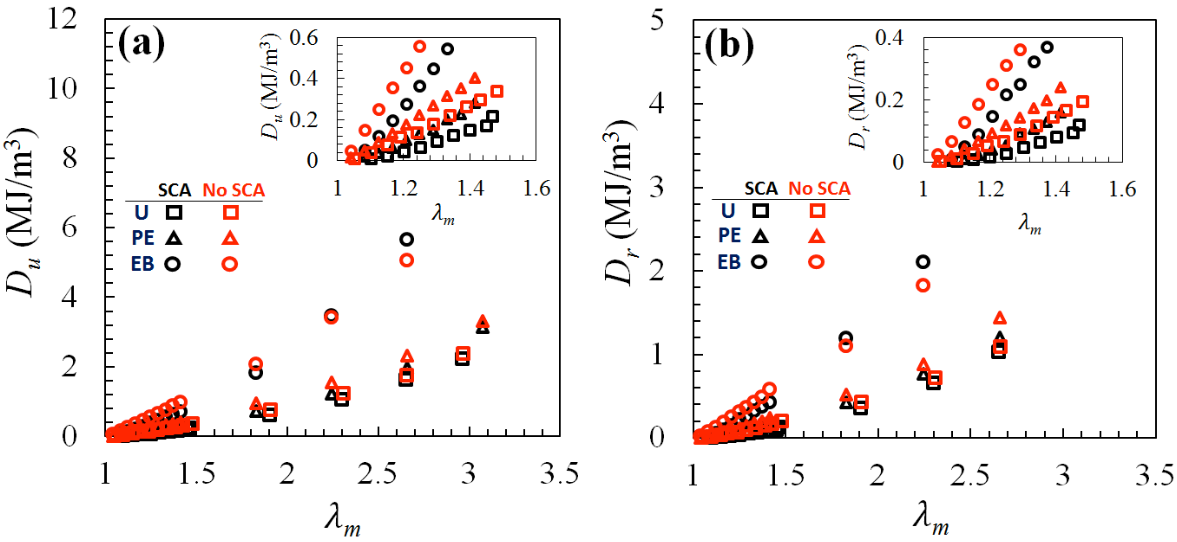

Fig. S4. Comparison of energy dissipation of (a) unloading (D_u) and (b) reloading (D_r) processes as a function of λ_m for SBR/silica of ϕ = 0.21 with and without SCA. The insets show the data in the small λ_m regime.

References

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