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Biaxial Tensile Behaviors of Elastomeric Polymer Networks

KOHJIYA Shinzo
Kyoto University, Institute for Chemical Research Uji, Kyoto 611-0011, Japan
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Ⅰ. Introduction

Among various mechanical properties, rubbery elasticity is reasonably of at most importance for elastomers. Elastic properties are generally to be described by the strain energy density function (W) of the material.[1-4] W is corresponding to free energy which determines the stress-strain relationship under deformation in general, and is a kind of rheological constitutive equations for describing elasticity. W is a function of the Green's invariants (I_i, i = 1, 2, 3) i.e. $W = W(I_1, I_2, I_3)$. When we are concerned with incompressible materials which include most of the elastomers, the volume does not change upon deformation may be neglected, i.e., $I_3 = (\lambda_1 \lambda_2 \lambda_3)^2 = (V/V_0)^2 = 1$. Hence

$$W = W(\lambda_1, \lambda_2) \quad (1)$$

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad (2)$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \quad (3)$$

where λ_i (i = 1, 2, 3) is the deformation ratio in each of 3 principal axes. The phenomenological expression of W is given by a polynominal function of $(I_1 - 3)$ and $(I_2 - 3)$ as

$$W(I_1, I_2) = \Sigma C_{ij} (I_1 - 3)^i (I_2 - 3)^j \quad (4)$$

where i and j are from 0 to ∞.

† 대표저자(*e-mail : kohjshin@scl.kyoto-u.ac.jp*)

Based on these considerations, experimental approaches to W have been conducted using biaxial tensile measurements.[4,5] However, number of such studies has been very small, although a recent book on rubbery elasticity emphasized the importance of W.[6] The reason may be experimental i.e. scarcity of multi-axial tensile instruments and difficulty or complexity in operating them. In contrast, uniaxial tensile testers have been so common that you can find it at almost every laboratory all over the world. Therefore, the experimental results of uniaxial tensile properties of elastomers abound and many theoretical treatments have been done on these data.[6-9] These situations have continued so long that the necessity of use of multiaxial results for the estimation of mechanical properties of elastomers has not

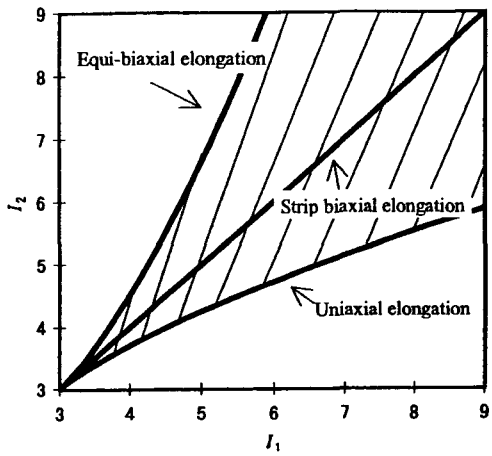

Figure 1. Experimental deformation range of I_1 and I_2 for incompressible materials.

been fully recognized in spite of the early publications. As seen from Figure 1, uniaxial elongational data are just on the borderline of the possible deformations of elastomers. For the estimation of W, which is to describe the stress-strain behaviors in general, it is necessary to conduct general biaxial elongation measurements or at least strip biaxial measurements. The latter may cover the central regions in the possible deformation area as shown in Figure 1.

In this report, the general biaxial tensile measurements have been carried out on end-linked poly (dimethylsiloxane) networks to show the elastic behaviors of a model polymer network. Also, to elucidate the effect of in-situ silica on natural rubber vulcanizates, they have been subject to strip biaxial tensile measurements.

Ⅱ. Theoretical background

The stain energy density function W represents the elastic free energy stored in a homogeneous, isotropic and elastic body under deformations. W for incompressible materials is expressed as described in Eqs. (1) through (4) using the Green's deformation tensors as two independent variables. The main objective of the present paper is to determine an appropriate set of terms as well as to assign values to the coefficients that can reproduce the stress-strain behaviors of the materials.

The derivatives of W, dW/dI_1 and dW/dI_2, are related with the principal stresses σ_i (i = 1, 2) under biaxial elongation in the 1 and 2 directions with σ_3 = 0 as follows:[2,3]

$$\frac{\partial W}{\partial I_1} = \frac{1}{2(\lambda_1^2 - \lambda_2^2)}\left[\frac{\lambda_1^3\sigma_1}{\lambda_1^2 - (\lambda_1\lambda_2)^{-2}} - \frac{\lambda_2^3\sigma_2}{\lambda_2^2 - (\lambda_1\lambda_2)^{-2}}\right] \quad (5)$$

$$\frac{\partial W}{\partial I_2} = \frac{-1}{2(\lambda_1^2 - \lambda_2^2)}\left[\frac{\lambda_1\sigma_1}{\lambda_1^2 - (\lambda_1\lambda_2)^{-2}} - \frac{\lambda_2\sigma_2}{\lambda_2^2 - (\lambda_1\lambda_2)^{-2}}\right] \quad (6)$$

where the stress σ is the nominal stress, i.e., the force per unit area before deformation. Variations of dW/dI_i on I_i are obtained by the biaxial stress (σ)-strain(λ) data; various sets of σ (σ_1 and σ_2) and λ (λ_1 and λ_2) were used to calculate W and I using the Eqs. (2), (3), (5) and (6).

Ⅲ. Experimentals

1. Materials

Two poly(dimethylsiloxane) network polymers (PDMS Gels) were prepared by end-linking hydrosilylation reaction between vinyl-terminated PDMS (Mn = 46,600) and tetrakis(dimethylsiloxy)silane (4 functional crosslinker) with and without solvent (oligo-PDMS of Mn = 3,000).[10] Natural rubber (NR, RSS No. 1) vulcanizates were prepared by usual procedures. NR compounded with a conventional silica (VN-3) was cured to afford VN vulcanizates. In-situ silica mixed with NR was prepared by the reported method using the sol-gel reaction.[11-14]

2. Measurements

General and strip biaxial tensile measurements were conducted on a biaxial stretching instrument BISS-0404 (Iwamoto Co.), which was designed in accord with that developed by Kawabata et al.[5,15]. The other measurements were reported.[10,14]

Ⅳ. Results and discussion

1. General Biaxial Elongation on Model PDMS Networks

The end-linked PDMSs were considered to be an elastomeric model polymer network, and subject to general biaxial measurement to determine the W. The results obtained on PDMS network obtained from 70 wt% solution are shown in Figure 2. It is seen that all the experimental points are on a plane except those at a very small strain region. From the plane we have estimated the W for this sample as follows:

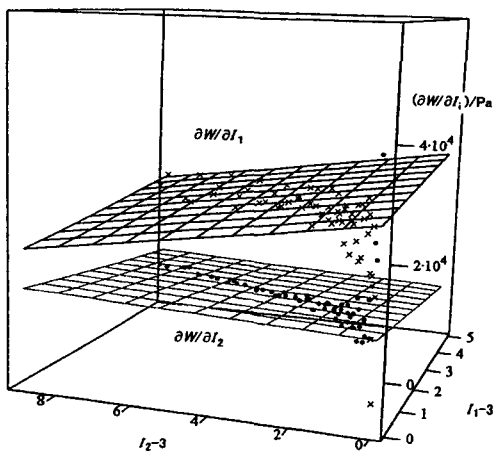

Figure 2. Derivative $\partial W/\partial I_1$ and $\partial W/\partial I_2$ as a function of (I_1-3) and (I_2-3) for the end-linked PDMS network prepared from 70 wt% solution. The upper and lower planes correspond to eqs 8 and 9.

$$W = \sum_{i,j=0}^{2} C_{ij}(I_1-3)^i(I_2-3)^j$$

$$= C_{10}(I_1\text{-}3) + C_{01}(I_2\text{-}3) + C_{11}(I_1\text{-}3)(I_2\text{-}3) + C_{20}(I_1\text{-}3)^2 + C_{02}(I_2\text{-}3)^2 \quad (7)$$

because each derivative of W of Eq. (7) is a linear function of each of (I_1 - 3) and (I_2 - 3) in the following:

$$\frac{\partial W}{\partial I_1} = C_{10} + C_{11}(I_2-3) + 2C_{20}(I_1-3) \quad (8)$$

$$\frac{\partial W}{\partial I_1} = C_{01} + C_{11}(I_1-3) + 2C_{02}(I_2-3) \quad (9)$$

From the plane in Figure 2, coefficients in Eq. (7) are determined. The calculated curves from the obtained W were found to reproduce the experimental results of uniaxial and equibiaxial strechings, which suggests the validity of the present W of the system.

2. Strip Biaxial Elongation on NR vulcanizate

NR vulcanizates compounded with VN-3 (conventional silica) and in-situ silica were subjected to uniaxial and strip biaxial stretching measurements. Figure 3 (a) and Figure 3 (b) show the strain (ε) dependences of stress (σ_1 and σ_2, respectively) under strip biaxial elongation. Both show a tendency

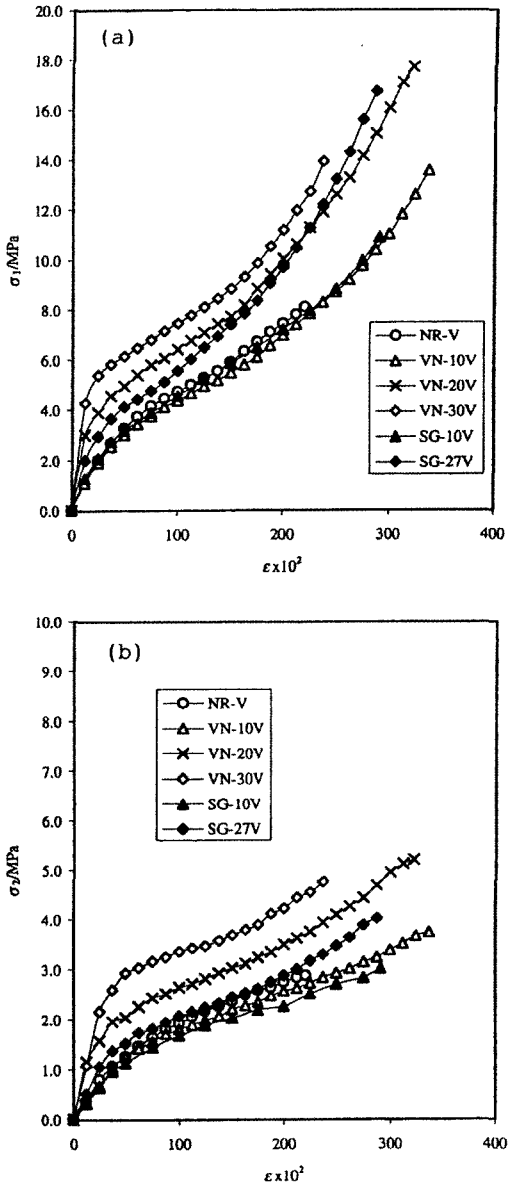

Figure 3. Strain (ε) dependence of stress under strip biaxial tensile mode. (a) the stress along the tensile axis (σ_1); (b) the stress along the fixed axis (σ_2).

that VN samples show higher moduli at the initial stage. This has been observed, and it is assumed that a conventional silica is much aggregated due to strong filler-to-filler interaction to form a pseudo network structure which contribute to modulus. In fact, this type of aggregation was observed by transmission electron microscopy (TEM). TEM on in-situ silica suggests much less aggregation. The W's estimated for silica mixed NR vulcanizates are expressed in the form of Eq.[10]

$$W = C_{10}(I_1\text{-}3) + C_{01}(I_2\text{-}3) + C_{20}(I_1\text{-}3)^2 \quad (10)$$

This W is appropriate at medium and large deformation regions, but more or less failed at initial stage of the elongation.

3. Reinforcement by In-situ Silica

For the comparison of reinforcement, it is better to compare the fillers of the same size. Fortunately, the present in-situ silica is almost of the same diameter as VN-3, which is observed by TEM. The differences of the two are already mentioned: those in initial moduli and TEM images suggesting more aggregation in VN-3. Figure 4 shows variation of two coefficient ratios C_{01}/C_{10} and C_{20}/C_{10}. The first term of Eq. (10) i.e. C_{10} represents the ideal rubber elasticity, thus the two ratios represent kinds of deviation from the ideal state. The results in Figure 4 may suggest the difference of the two silicas in affecting the ideal rubbery behavior of NR vulcanizates. The in-situ silica may be assumed to have moderate filler-to-filler and filler-to-rubber interactions which contribute to the reinforcement somewhat differently from a conventional precipitated silica (in this case VN-3).

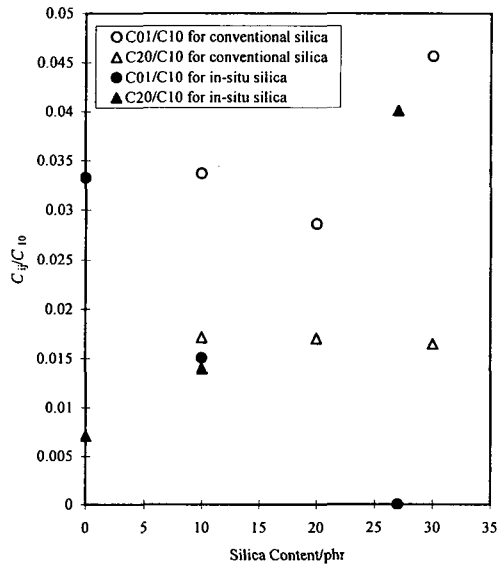

Figure 4. Dependence of C_{01}/C_{10} and C_{20}/C_{10} on the silica contents in phr.

V. Summary

For the total description of mechanical behaviors of elastomers, it is necessary to know the so-called rheological constitutive equation *i.e.* the strain-energy density function (W) in case of elastomers, which necessitates biaxial tensile results of elastic body. This paper first describes the experimental results of biaxial tensile measurements on poly (siloxane) model networks. W was estimated from its differential form *i.e.* the 1st differential of W is stress. The W was found to reproduce the experimental stress-strain results, and the W estimated for silica filled poly(siloxane) networks suggest a different behavior between conventional precipitated silica and *in situ* formed silica. The difference suggests the different surface property of the two silicas.

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