Biaxial Deformation Behavior of Polymer Networks

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Introduction

Biaxial elongation experiments provide us a lot of information on an elastic potential of polymer networks. The elastic potential is usually called the strain energy function W, and the stress-strain relation can be calculated by using derivatives of W. So far many studies, both by experiment and theory, have been made to establish the framework of W, but little is known on the functional form of W even at present [1]. The classical theory of rubber elasticity, built up on the basis of the statistical mechanics, has shown that the elasticity of rubbers has an entropic origin. The theory often uses the assumption that rubbers are incompressible to obtain the stress-strain relation. The applicability of this assumption is, of course, supported by experiments but has no theoretical basis. Most of recent studies tend to refine the entropic nature of the elasticity; thus, the issue on incompressibility remains still unsolved. The incompressibility must be closely related to the fact that rubbers have a finite, *i. e.*, non-zero, volume at rest, which cannot be described by the Gaussian chains used in the statistical theory. Phenomenological approach to W also has a long history. Because rubbers can be stretched to large strains, the finite deformation theory is used to describe the stress-strain relation of the materials. In this theory, W is usually regarded as a function of I_1, I_2 and I_3, with I_i being the i-th invariant of the deformation tensor. The finite deformation theory itself, however, cannot determine the functional form of W, although the theory may impose several requirements to be satisfied on W. It has been reported that the derivatives of W with respect to the invariants show strange behavior at small strains and the behavior cannot be explained by any of the current theoretical models. In this paper we focus on the anomalous behavior of the derivatives at small strains.

Models for Strain Energy Function

Until now various models are presented for W, and among them the most general expression is known to be the following form [1].

$$W = \sum_{l,m,n} C_{lmn}(I_1-3)^l(I_2-3)^m(I_3-1)^n \tag{1}$$

Here, C_{lmn} is the constant and the parameters for the summation over l, m, and n should be positive integers. The invariants (I_1, I_2 and I_3) are respectively defined by

$$I_1 = \lambda_1^2+\lambda_2^2+\lambda_3^2$$
$$I_2 = \lambda_1^2\lambda_2^2+\lambda_2^2\lambda_3^2+\lambda_3^2\lambda_1^2$$
$$I_3 = \lambda_1^2\lambda_2^2\lambda_3^2$$

where, λ_i is the principal stretch ratio in the i-th (i = 1, 2, 3) direction. When materials can be assumed to be incompressible, I_3 = 1, Equation (1) is reduced to

$$W = \sum_{l,m} C_{lm}(I_1-3)^l(I_2-3)^m \tag{2}$$

One of the special forms of the above equation is

$$W = C_1(I_1-3) \tag{3}$$

This is identical to the expression obtained from the classical theory of rubber elasticity (a Gaussian model) if $C_1 = C_{10} = G/2$, with G being the shear modulus. Another simplified form shown below, known as the Mooney model, is often used to analyze stress-strain behavior of real elastomers.

$$W = C_1(I_1-3)+C_2(I_2-3) \tag{4}$$

Here, $C_1 = C_{10}$ and $C_2 = C_{01}$.

There exist more complicated forms: for example, the following expression is proposed for W by Beda [2].

$$W = \sum_p \frac{A_p}{\alpha_p}(I_1-3)^{\alpha_p} + \sum_q \frac{B_q}{\beta_q}(I_2-3)^{\beta_q} \tag{5}$$

Here, A_p and B_q are constants, and the exponents (α_p and β_q) are positive and allowed to be non-integers.

Derivatives of the Strain Energy Function

According to the Mooney model, the derivatives of W with respect to I_i are given as follows.

$$\frac{\partial W}{\partial I_1} = C_1, \quad \frac{\partial W}{\partial I_2} = C_2 \tag{6}$$

This set of derivatives also include the expression for the Gaussian model as a special case of $C_1 = G/2$ and $C_2 = 0$.

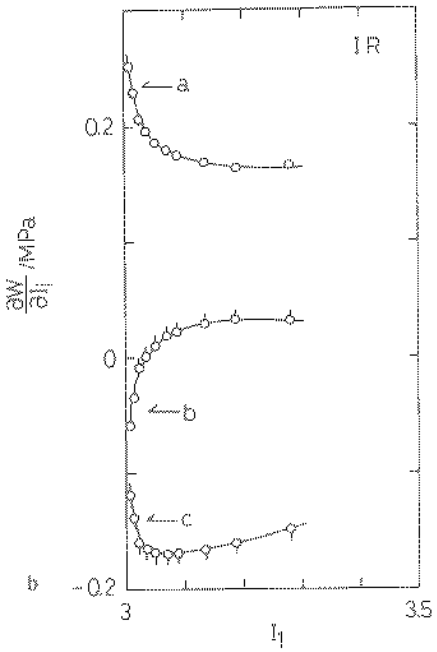

Figure 1. $\partial W/\partial I_i$ vs. I_1 for an isoprene rubber. Upper; $\partial W/\partial I_1$: middle; $\partial W/\partial I_2$: bottom; $\partial W/\partial I_3$.

Figure 1 shows $\partial W/\partial I_i$ plotted against I_1 under pure shear deformation for an isoprene rubber (IR). The original data for the plots were those reported by Kawabata et al., and we reanalyzed the data as a compressible material using the reported Poisson ratio [3,4]. According to the simple model (for example, Equation (6)), the derivatives not only with respect to I_1 but also I_2 are independent of I_1. However, the curve of $\partial W/\partial I_1$ in the figure shows an upturn at small strains (i. e., $I_3 \approx 3$), $\partial W/\partial I_2$ showing a downturn. The curve of $\partial W/\partial I_3$ also behaves in a complicated manner. As stated above, the simple model cannot explain the experimental data near $I_3 = 3$. We may call the upturn and downturn, together with the complicated change for the $\partial W/\partial I_3$ curve, anomalous behavior of the derivatives, although the behavior was not observed in the pioneering work made by Rivlin and Saunders [1]. At present it is well known that the anomalous behavior is widely observed for other network materials than IR: another example will be shown later. Beda tried to explain the anomalous behavior based on his model (Equation (5)). At very small strains, W for incompressible materials can be approximated by using α_1 (< 1) and β_1 (< 1) as [2]

$$W = \frac{A_1}{\alpha_1}(I_1-3)^{\alpha_1} + A_2(I_1-3)+\frac{B_1}{\beta_1}(I_2-3)^{\beta_1} \tag{7}$$

This gives the derivatives of

$$\frac{\partial W}{\partial I_1} = \frac{A_1}{(I_1-3)^{1-\alpha_1}} + A_2, \quad \frac{\partial W}{\partial I_2} = \frac{B_1}{(I_2-3)^{1-\beta_1}} \tag{8}$$

These can describe the upturn and downturn behavior as strains approach to zero if $A_1 > 0$ and $B_1 < 0$. However, the zero-strain state is becomes a singularity; in this sense, Equation (7) is improper for W.

Limiting Values of the Derivatives at Zero-Strain Limit

As briefly reviewed in the previous section, real elastomers show the anomalous behavior in the plots of $\partial W/\partial I_i$ vs. I_i at zero-strain limit, and no models exist capable to explain the strange behavior at present.

Even in this situation, the limiting values of the derivatives at zero-strain limit can be evaluated if we assume that W in the finite deformation theory should coincide with that in the linear elasticity theory at the zero-strain limit.

Looking back to the linear elasticity theory, W for compressible materials can be uniquely written with bulk modulus K and G as

$$W = \left(\frac{K}{2} + \frac{2G}{3}\right) J_1^2 - 2GJ_2 \qquad (9)$$

if we use the following three invariants of the infinitesimal strain tensor.

$$J_1 = \lambda_1 + \lambda_2 + \lambda_3 - 3$$
$$J_2 = (\lambda_1 - 1)(\lambda_2 - 1) + (\lambda_2 - 1)(\lambda_3 - 1) + (\lambda_3 - 1)(\lambda_1 - 1)$$
$$J_3 = (\lambda_1 - 1)(\lambda_2 - 1)(\lambda_3 - 1)$$

As Equation (9) leads to the limiting values at zero-strain of

$$\lim_{J_i \to 0} \frac{\partial W}{\partial J_1} = 0$$
$$\lim_{J_i \to 0} \frac{\partial W}{\partial J_2} = -2G$$
$$\lim_{J_i \to 0} \frac{\partial W}{\partial J_3} = 0$$

and then I_i is related to J_i as

$$I_1 = J_1^2 + 2J_1 - 2J_2 + 3$$
$$I_2 = 2J_1^2 + J_2^2 + 2J_1J_2 - 2J_3J_1 + 4J_1 - 6J_3 + 3$$
$$I_3 = (1 + J_1 + J_2 + J_3)^2$$

we have for the limiting values of the derivatives with respect to I_i [4,6]

$$\lim_{I_1, I_2 \to 3; I_3 \to 1} \frac{\partial W}{\partial I_1} = \frac{5G}{8} \qquad (10a)$$

$$\lim_{I_1, I_2 \to 3; I_3 \to 1} \frac{\partial W}{\partial I_2} = -\frac{G}{8} \qquad (10b)$$

$$\lim_{I_1, I_2 \to 3; I_3 \to 1} \frac{\partial W}{\partial I_3} = -\frac{3G}{8} \qquad (10c)$$

The arrows a, b and c in Figure 1 indicate the calculated limiting values with respect to I_1, I_2 and I_3, respectively. Here, G used was the reported value for the isoprene rubber. The predicted values are in good agreement with the experimental ones.

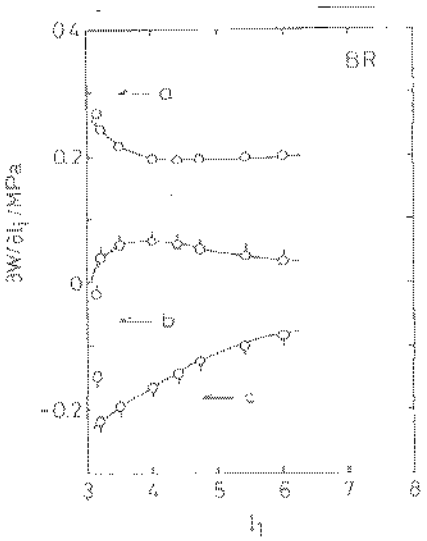

Figure 2. $\partial W/\partial I_i$ vs. I_1 for a butadiene rubber. Upper; $\partial W/\partial I_1$: middle; $\partial W/\partial I_2$: bottom; $\partial W/\partial I_3$.

Figure 2 shows similar plots for a butadiene rubber (BR) obtained under pure shear deformation [5,6]. The original data were reported by Fukahori et al [5]. The anomalous behavior is also observed for BR. The limiting values calculated by Equation (10) are indicated by the arrows and the arrows have the same as those in Figure 1. The agreement between experiment and theory is also fairly good for BR. Similar results have been obtained for other types of rubbers.

Conclusions

Real elastomers show the anomalous behavior in the I_i dependence curves of the derivatives of W with respect to I_i at small strains. The limiting values of the derivatives were evaluated by a simple model based on the assumption that W in the large deformations should coincide with that in the linear elasticity theory. The calculated values were in good agreement with the experimental ones for real elastomers.

References

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