Strain Energy Function of Poly(Propylene Oxide) and Polybutadiene Elastomers Estimated by General Biaxial Strain Testing[†]

by

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Stress-strain relations of poly(propylene oxide) (PPO) and polybutadiene (PB) elastomers are investigated by general biaxial strain testing where the strains in two orthogonal directions are varied independently. The data for general biaxial deformation provide an unambiguous basis to estimate the form of strain energy function (W) governing the stress-strain relations of elastomers. The function $W(I_1, I_2) = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + C_{11}(I_1 - 3)(I_2 - 3) + C_{20}(I_1 - 3)^2 + C_{02}(I_2 - 3)^2$, where I_1 and I_2 are the first and second invariants of Green's deformation tensor and C_{ij} ($i, j = 0, 1, 2$) are the numerical coefficients, satisfactorily describes the data in the whole range of biaxial strain for the two elastomers.

Key words : *Elastomers, Rubber, Rubber elasticity, Strain energy function, Stretching*

1 Introduction

Elastomers (rubbers) are a unique solid material which exhibits high recoverable deformability due to entropic elasticity.^{1), 2)} Elastomers occupy an important place among various industrial materials due to their characteristic mechanical properties. The stress-strain relations of elastomers become considerably nonlinear under large deformation. Strain energy function (W), which is equivalent to elastic free energy, governs the nonlinear stress-strain relations of elastomers under all types of deformation. The true forms of W have long received much attention from both academic and industrial viewpoints. The finite element method (FEM) for rubber products is becoming very popular in industrial researches, because FEM is a powerful tool to predict the behavior under complicated deformation. The reliability of FEM primarily relies on that of W employed in the simulation. A lot of phenomenological forms of W have been proposed.²⁾ The stress-strain data for many types of deformation are required to estimate unambiguously the form of W and the values of the model parameters.³⁾ The estimation of W relying on simple uniaxial deformation often leads to incorrect conclusion, which is a corollary of the fact that it is only a particular one among all physically accessible deformations of elastomers. General biaxial strain testing, which varies independently the strains in the two orthogonal directions, is a useful technique to achieve many types of deformation. In principle, general biaxial strain is capable of covering all types of homogeneous deformation for incompressible elastomers. We have characterized the forms of W for polydimethylsiloxane (PDMS) elastomers⁴⁾ and several

types of polymer gels^{5), 6)} on the basis of the general biaxial stress-strain data. The W expressed by a quadratic function of the first and second strain invariants including their cross-term satisfactorily described the data in the entire strain range for the PDMS elastomers.⁴⁾ However, the reports for general biaxial strain testing of elastomers are quite limited due to the experimental difficulties, and it also remains to be studied how universal this W is for various elastomers. The present work investigates the biaxial stress-strain behavior of the two elastomers with different constituent polymers, i.e., poly(propylene oxide) and polybutadiene elastomers. We discuss the form of W to reproduce the data. The results of the present study will significantly contribute to the full understanding of rubber elasticity, and provide important information about W .

2 Materials and Sample Preparation

The poly(propylene oxide) (PPO) and poly(butadiene) (PB) elastomers were prepared by end-linking the corresponding end-reactive precursor polymers with multi-functional cross-linkers. The three-arm star shaped PPO with hydroxyl group at each chain end (Mitsui Chemical Co.) and the linear PB with hydroxyl groups at both ends (Idemitsu Kosan Co.) were employed as the precursor polymers. The number-average molecular weights of the PPO and PB precursor polymers were 1.0×10^4 and 3.0×10^3 , respectively. For the PPO and PB elastomers, *m*-xylene disocyanate and tris (4-isocyanatophenyl) thiophosphate were used as cross-linkers, respectively. The square sheet specimens of the PPO and PB elastomers ($50 \times 50 \times 1.1$ mm) for the biaxial stretching experiments were obtained by the cross-link-

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ing reaction at 65°C for five hours. The samples for uniaxial deformation ($50 \times 5 \times 1.1\text{mm}$) were cut out from the sheet specimens.

3 Measurements

The biaxial stretching experiments were performed at room temperature with a custom-built biaxial tester BIS-0404, and the details of the experiments were described elsewhere.⁴⁾ The uniaxial stretching measurements were made at room temperature with an Orientec Tensilon RTM-500. The three types of stretching deformation (Fig. 1), i.e., uniaxial, equi-biaxial and two-step stretching, were employed. In the two-step stretching, the specimen was first elongated up to 100% strain with maintaining zero strain in one direction (i.e., planar stretching), and thereafter it was elongated in the direction, which had been the constrained direction in the first stage, until the equi-biaxially stretched state with 100% strain was achieved. In each deformation, the crosshead speed was 0.1mm/s, and it was sufficiently slow to obtain the equilibrium stress without time effect. In the preliminary experiments, each specimen exhibited rupture at an equi-biaxial strain of ca. 120%. The maximum strain in each stretching mode was set to be 100% because the same specimen was employed for all types of deformation. Before the measurements, the specimens were equi-biaxially elongated to 100% strain and the imposed strain was completely released. This cycle was repeated twice prior to the collection of the stress-strain data. This pretreatment was made to obtain the data with high reproducibility.

4 Results and Discussion

Figures 2-4 show the nominal stress (σ)–stretch ratio (λ) relations for uniaxial, equi-biaxial, and two-step stretching for the PB elastomer, respectively. Figures 5-7 illustrate the corresponding data for the PPO elastomer. For equi-biaxial stretching, the figures include the data in one direction, because no appreciable difference in the stresses in the two stretching directions was observed. For both samples, σ_x and σ_y become identical in the equi-biaxially stretched state of $\lambda_x = \lambda_y = 2$ after the two-step

Fig. 1 Schematics of employed deformation modes.

Fig. 2 Nominal stress-stretch ratio relation for uniaxial stretching of PB elastomer. The black solid line represents the curve calculated from Eq. (1).

Fig. 3 Nominal stress-stretch ratio relation for equi-biaxial stretching of PB elastomer. The black solid line represents the curve calculated from Eq. (1).

Fig. 4 Nominal stress-stretch ratio relation for two-step stretching of PB elastomer. The black solid lines represent the curves calculated from Eq. (1).

Fig. 5 Nominal stress-stretch ratio relation for uniaxial stretching of PPO elastomer. The black solid line represents the curve calculated from Eq. (1).

Fig. 6 Nominal stress-stretch ratio relation for equibiaxial stretching of PPO elastomer. The black solid line represents the curve calculated from Eq. (1).

Fig. 7 Nominal stress-stretch ratio relation for two-step stretching of PPO elastomer. The black solid lines represent the curves calculated from Eq. (1).

stretching. This evidently shows that the strain history has no appreciable effect on the stress-strain behavior in the equilibrium state.

The stress-strain relation in each deformation was linear only in the small strain region of $\lambda_x < 1.1$, and the strain-softening behavior was observed in the larger strain region. The slope in the region of $\lambda_x < 1.1$ corresponds to the initial modulus in each deformation. According to linear elasticity theory,⁷⁾ the slopes in equibiaxial and uniaxial stretching, and those in the stretching and constrained directions in planar stretching are $6G$, $3G$, $4G$ and $2G$ for incompressible materials, respectively, where G is the shear modulus. Almost the same relation between different types of deformation was observed for both elastomers, and the values of G were evaluated to be 1.9×10^4 and 2.1×10^4 Pa for the PB and PPO elastomers, respectively. Since the two elastomers have almost the same values of G , they are almost similar in the amount of elastically effective cross-links.

Our previous study^{4), 5)} showed that the following W function successfully described the biaxial data in the entire strain range for the PDMS elastomers :

$$W(I_1, I_2) = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + C_{11}(I_1 - 3)(I_2 - 3) + C_{20}(I_1 - 3)^2 + C_{02}(I_2 - 3)^2 \quad (1)$$

where C_{mn} ($m, n = 0, 1, 2$) are the numerical coefficients, and I_i ($i = 1, 2$) are the first and second invariants of the Green's deformation tensor defined as

$$I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2 = \lambda_x^2 + \lambda_y^2 + (\lambda_x \lambda_y)^{-2} \quad (2a)$$

$$I_2 = \lambda_x^2 \lambda_y^2 + \lambda_y^2 \lambda_z^2 + \lambda_z^2 \lambda_x^2 = \lambda_x^2 + \lambda_x^{-2} + \lambda_y^{-2} \quad (2b)$$

with $\lambda_x \lambda_y \lambda_z = 1$ for incompressibility. Equation (1) corresponds to a version of polynomial expansion form of I_1 and I_2 :^{1), 2)}

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

with $C_{00} = 0$. The function composed of only the linear terms of I_1 and I_2 is well known as Mooney function :^{1), 2)}

$$W(I_1, I_2) = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) \quad (4)$$

It has long been known that Eq. (4) apparently fits the uniaxial stress-strain data. However, Eq. (4) obviously fails to describe the biaxial data,^{4), 8)} indicating that it is far from the true form of W . The failure of the Mooney function in the biaxial deformation has been demonstrated so far for several rubbers^{4), 8)} and highly swollen gels,⁵⁾ and the same result was confirmed for the PPO and PB elastomers examined in present work, the details of which are not described here.

The nominal stresses σ_x and σ_y in general biaxial deformation are straightforwardly obtained as the derivative of W with respect to λ_x and λ_y , respectively :

$$\sigma_x = \frac{2}{\lambda_x} \left(\lambda_x^2 - \frac{1}{\lambda_x^2 \lambda_y^2} \right) \left(\frac{\partial W}{\partial I_1} + \lambda_y^2 \frac{\partial W}{\partial I_2} \right) \quad (5a)$$

$$\sigma_y = \frac{2}{\lambda_y} \left(\lambda_y^2 - \frac{1}{\lambda_x^2 \lambda_y^2} \right) \left(\frac{\partial W}{\partial I_1} + \lambda_x^2 \frac{\partial W}{\partial I_2} \right) \quad (5b)$$

Each derivative of Eq. (1) is given as

$$\partial W / \partial I_1 = C_{10} + C_{11}(I_2 - 3) + 2C_{20}(I_1 - 3) \quad (6a)$$

$$\partial W / \partial I_2 = C_{01} + C_{11}(I_1 - 3) + 2C_{02}(I_2 - 3) \quad (6a)$$

We assess the applicability of Eq. (1) to the biaxial stress-strain data of the PB and PPO elastomers. The fitting of Eq. (5) with Eq. (6) to the data in each deformation was made, and the fitted value of each coefficient was summarized in Table 1. The black solid lines in each figure correspond to the fitting results. The calculated curves well reproduce the data in each deformation in the entire strain range for both elastomers. All five terms in Eq. (1) were required to obtain the satisfactory fit: If any one of C_{11} , C_{20} and C_{02} was zero, the quality of the resultant fitting was unsatisfactory. The coefficients of the high order terms (in particular C_{02}) are more than one order of magnitude smaller than those of the linear terms (C_{10} and C_{01}), but it should be noted that the contributions of the high order terms become pronounced at high strain where I_1 and I_2 are very large. For both elastomers, the values of C_{11} are negative, which was also observed for the PDMS elastomers.⁴⁾ However, the stresses calculated from Eq. (1) with the two sets of the coefficients (Table 1) always increase with an increase in strain, which also holds beyond the maximum strain examined here. This means that the two sets of the coefficients obtained here does not violate the physical stability of W , although the values of C_{11} are negative.

The physical or molecular interpretation of each coefficient is not straightforward, because the character of Eq. (1) is phenomenological. The contributions of the terms excepting the first term ($I_1 - 3$) have been attributed to the deviation of real elastomers from ideal polymer networks,^{1), 2)} because W composed of only ($I_1 - 3$) term (Neo-Hookean model) is theoretically derived for ideal networks made of Gaussian polymer chains with infinite extensibility and with no topological interaction between other chains. The general biaxial strain testing for the elastomers with varying systematically the length of network strands and the concentration of cross-links may elucidate how each topological feature of rubbery net-

works influences the contribution of each term in Eq. (1). This is a subject in our future study.

The present work showed that Eq. (1), which was originally proposed for the PDMS elastomers,⁴⁾ was also valid as a phenomenological form of W with high accuracy for the PPO and PB elastomers. This result suggests that Eq. (1) will be applicable to describe the large deformation behavior for various conventional elastomers independently of the constituent polymers.

5 Conclusions

The stress-strain data under general biaxial deformation for the PPO and PB elastomers were obtained to provide a definite basis to estimate the true form of the strain energy function (W). The function $W(I_1, I_2) = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + C_{11}(I_1 - 3)(I_2 - 3) + C_{20}(I_1 - 3)^2 + C_{02}(I_2 - 3)^2$ successfully described the stress-strain relations in the whole range of biaxial strain for the two elastomers examined here and the PDMS elastomers studied earlier. This phenomenological W is expected to describe the large deformation behavior of various elastomers independently of the constituent polymers.

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Table 1 Coefficients of Eq. (1) for each elastomer.

	C_{10} (Pa)	C_{01} (Pa)	C_{11} (Pa)	C_{20} (Pa)	C_{02} (Pa)
PB	3.27×10^4	5.60×10^3	-6.30×10^2	3.00×10^2	4.00×10^1
PPO	3.85×10^4	3.65×10^3	-6.70×10^2	4.00×10^2	9.65×10^1