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Quantitative Analysis of the Strain Energy Density Function for *cis*-1,4-Polyisoprene Rubber Vulcanizate

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ABSTRACT: A quantitative analysis of the strain energy density function for an isoprene rubber vulcanizate is carried out based on the experimental biaxial stress–strain data presented in a previous paper. The form of the strain energy density function is $W = CT(I_1 - 3) + \beta(I_1,I_2)$, which was derived in the previous paper by measuring its derivative forms with respect to I_1 and I_2, the first and second invariants of the deformation tensor. First, the stresses along the two principal directions are integrated to evaluate the strain energy density as a function of I_1 and I_2; then the function $\beta(I_1,I_2)$ is determined based on the functional form of W given above. It is observed that the function $\beta(I_1,I_2)$ represents between 0.32 and 0.46 of the total energy W for all deformations examined in this experiment and that it decreases with increasing deformation such that, for example, the amount is 0.41 at $I_1 = I_2 = 5$ and 0.36 at $I_1 = I_2 = 10$ in the case of pure shear deformation. In order that this result can be compared with those of other researchers, the ratio f_e/f (where f is the uniaxial tensile stress and f_e is the energetic component which is considered to be caused by the internal energy change accompanying the deformation) is derived from the biaxial experiment and discussed.

Introduction

In an earlier paper,[1] an expression for the strain energy density function, W, for a vulcanized *cis*-1,4-polyisoprene rubber was developed from an experimental survey in which a biaxial extension technique was used. The function W presented has a simple form comprising two separate terms, one term directly proportional to absolute temperature, the other, independent of temperature; the latter is a complicated function of the deformation as shown in eq 1:

$$W = CT(I_1 - 3) + \beta(I_1,I_2) \qquad (1)$$

Here C is a constant, T is the absolute temperature, and $\beta(I_1,I_2)$ is a function only of deformation expressed by I_1

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and I_2, which are, respectively, the first and second invariants of Green's deformation tensor and functions of, the principal stretch ratios λ_i ($i = 1, 2, 3$):

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \tag{2a}$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \tag{2b}$$

The first term on the right-hand side of eq 1 has the same form as that of the strain energy density function derived from the classical theory of rubber elasticity.[2,3] Therefore, this term is considered to be a component of the strain energy density caused by the entropy change due to deformation of the chain molecules. On the other hand, the second term is a new energy term which, to date, has not been explained by molecular theory.

In the previous paper, only the derivative forms of the function $\beta(I_1,I_2)$ with respect to I_1 and I_2 were introduced because the derivative forms are obtained directly from the measurement of stresses under biaxial extension. In the present paper, a quantitative analysis of the β function is carried out on the basis of the experimental data which have been presented in the previous paper, and the ratio of the magnitude of the function $\beta(I_1,I_2)$ to the total strain energy density $W(I_1,I_2)$ is discussed.

Thermodynamic Consideration and the Method for the Quantitative Determination of the Function $\beta(I_1,I_2)$

1. Analysis of the Thermodynamic Meaning of the β Function. It is well-known that the change in the Helmholtz free energy, A (per unit volume of the medium), associated with the deformation of an incompressible and elastic body under isothermal conditions is equal to the work done on the system and that this work is equal to the strain energy density W stored in the body. From the thermodynamic relations, the following equations are derived:

$$(\partial W/\partial I_1)_{I_2,T} = (\partial A/\partial I_1)_{I_2,T} = (\partial U/\partial I_1)_{I_2,T} - T(\partial S/\partial I_1)_{I_2,T} \tag{3a}$$

$$(\partial W/\partial I_2)_{I_1,T} = (\partial A/\partial I_2)_{I_1,T} = (\partial U/\partial I_2)_{I_1,T} - T(\partial S/\partial I_2)_{I_1,T} \tag{3b}$$

where U is the internal energy and S is the entropy of the system. The following is also derived based on constant-volume thermodynamic relations such that

$$\mathrm{d}A = -S\,\mathrm{d}T + \frac{\partial W}{\partial I_1}\,\mathrm{d}I_1 + \frac{\partial W}{\partial I_2}\,\mathrm{d}I_2 \tag{4}$$

By differentiating eq 4, one obtains

$$(\partial A/\partial I_1)_{I_2,T} = \partial W/\partial I_1 \tag{5a}$$

$$(\partial A/\partial I_2)_{I_1,T} = \partial W/\partial I_2 \tag{5b}$$

$$(\partial A/\partial T)_{I_1,I_2} = -S \tag{5c}$$

According to Maxwell's relation of partial differentiation, eq 6 and 7 derive from eq 5a and 5c and eq 5b and 5c, respectively:

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial W}{\partial I_1}\right)\right]_{I_1,I_2} = -\left(\frac{\partial S}{\partial I_1}\right)_{I_2,T} \tag{6}$$

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial W}{\partial I_2}\right)\right]_{I_1,I_2} = -\left(\frac{\partial S}{\partial I_2}\right)_{I_1,T} \tag{7}$$

Substituting eq 6 into eq 3a, and eq 7 into eq 3b, one obtains

$$\left(\frac{\partial U}{\partial I_1}\right)_{I_2,T} = \left(\frac{\partial W}{\partial I_1}\right)_{I_2,T} - T\frac{\partial}{\partial T}\left[\left(\frac{\partial W}{\partial I_1}\right)\right]_{I_1,I_2} \tag{8}$$

$$\left(\frac{\partial U}{\partial I_2}\right)_{I_1,T} = \left(\frac{\partial W}{\partial I_2}\right)_{I_1,T} - T\frac{\partial}{\partial T}\left[\left(\frac{\partial W}{\partial I_2}\right)\right]_{I_1,I_2} \tag{9}$$

From substitution of the functional form of W of eq 1 into eq 8 and 9, it follows that

$$(\partial U/\partial I_1)_{I_2,T} = \partial\beta(I_1,I_2)/\partial I_1 \tag{10}$$

$$(\partial U/\partial I_2)_{I_1,T} = \partial\beta(I_1,I_2)/\partial I_2 \tag{11}$$

Therefore

$$U - U_0 = \beta(I_1,I_2) \tag{12}$$

where U_0 is the internal energy of the system in the undeformed state and U is the internal energy in the deformed state. Also, we obtain

$$-T(\partial S/\partial I_1)_{I_2,T} = CT \tag{13}$$

$$-T(\partial S/\partial I_2)_{I_1,T} = 0 \tag{14}$$

Thus, the first term on the right-hand side of eq 1 is considered to be related to the entropy change of the deformed system. On the other hand, the contribution of the internal energy change of the system to the strain energy density can be represented by the second term shown by the function β, provided that β is independent of temperature (as has been found by our previous experiment).

For the thermodynamic analysis, the volume change of the samples must be taken into account since the experiment has been carried out at constant atmospheric pressure. The volume expansion accompanied by deformation was, however, confirmed to be negligibly small by our previous experiment, and the effect of thermal expansion on the resultant magnitude of the β function is considered to be small compared with the magnitude of the β function (which has been obtained from our experiment). Therefore, according to Gee's approximation,[4] the effect of thermal expansion has been ignored in the thermodynamic analysis discussed above.

2. Evaluation of the β Function. The strain energy density stored in a body under incompressible and isothermal deformation may be evaluated in two ways: (i) by integration of $\partial W/\partial I_1$ and $\partial W/\partial I_2$, which are determined from experimentally observed stress–strain relations under biaxial deformation, or (ii) by direct integration of the forces applied to the body during deformation. For the evaluation of the magnitude of the W function, the latter method seems sufficiently accurate. For biaxial deformation of an elastic body, the strain energy density function W is given by the integration

$$W = \sum_{i=1}^{2}\int_1^{\lambda_i}\sigma_i\,\mathrm{d}\lambda_i \tag{15}$$

where σ_i and λ_i ($i = 1, 2$) are the principal stress and the principal stretch ratio along the ith principal axis, respectively. The stresses used here are engineering stresses and refer to the unstrained dimensions. The value of W obtained by eq 15 as a function of λ_i can be rewritten in terms of I_1 and I_2 by means of eq 2. Evaluation of the function β is now possible by using the following equation, as C has already been determined by experiment:

$$\beta(I_1,I_2) = W(I_1,I_2) - CT(I_1 - 3) \tag{16}$$

The integration in eq 15 was carried out under several deformation modes by means of numerical methods. The strain ratio is denoted by k such that

$$k = \frac{\epsilon_2}{\epsilon_1} = \frac{\lambda_2 - 1}{\lambda_1 - 1} \qquad (\epsilon_1 \geq \epsilon_2) \tag{17}$$

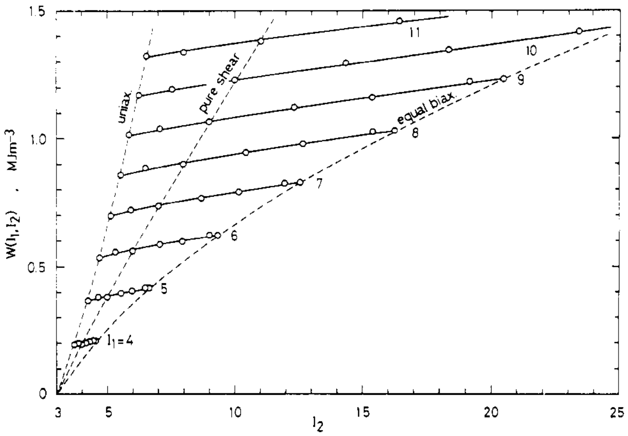

Figure 1. Plot of the strain energy density function $W(I_1,I_2)$ against I_2 at constant I_1 for isoprene rubber vulcanizate at 293 K.

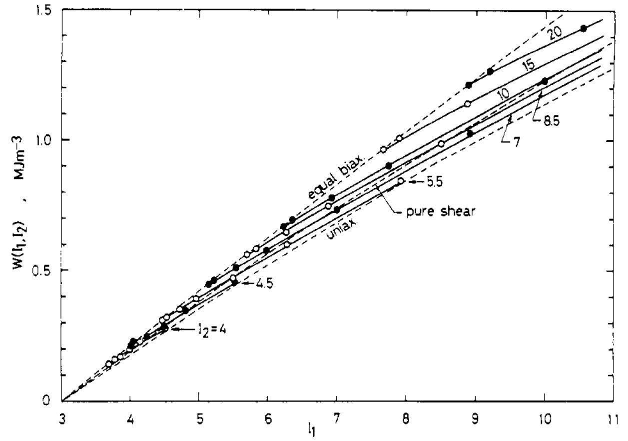

Figure 2. Plot of $W(I_1,I_2)$ against I_1 at constant I_2.

The procedure is as follows. A biaxial stress–strain relation under a constant strain ratio k is redrawn from the 5-min isochronal data of the stress–strain relations obtained by biaxial stress relaxation data for various biaxial deformations (as shown in Figures 4 and 5 of the previous paper).[1] These data are considered to be obtained in a near-equilibrium state. The integration of eq 15 becomes

$$W = \int_1^{\lambda_1} (\sigma_1 + k\sigma_2)\, d\lambda_1 \tag{18}$$

where the biaxial stresses, σ_1 and σ_2, may be expressed as a function of only one variable, λ_1, using a constant parameter k. The integration in eq 18 is then carried out for the deformation modes associated with various k values to evaluate the function W as a function of deformation. The case of $k = 1$ represents equal biaxial (equibiaxial) extension, while $k = 0$ represents pure shear. Only in the case of uniaxial deformation is k not constant, but the integration is done only for σ_1 of the tensile stress.

Results

The quantitative presentation of the strain energy density function W at 293 K is shown in Figures 1 and 2 as a function of I_1 and I_2. As mentioned previously, the value of the W function is obtained by integrating stresses for several deformation modes of different k's at the points plotted on these figures. In the same manner, the values of the function $\beta(I_1,I_2)$ at 293 K are plotted in Figures 3 and 4. As seen from these figures, the form of the function β depends on both I_1 and I_2. A contour diagram of the function β is illustrated in Figure 5 to facilitate the observation of its functional form. When one draws a similar diagram for the first term of eq 1, the contour lines should be parallel to the I_2 axis. However, the contour lines of $\beta(I_1,I_2)$ are inclined to the I_2 axis and it seems that these lines are nearly parallel to each other.

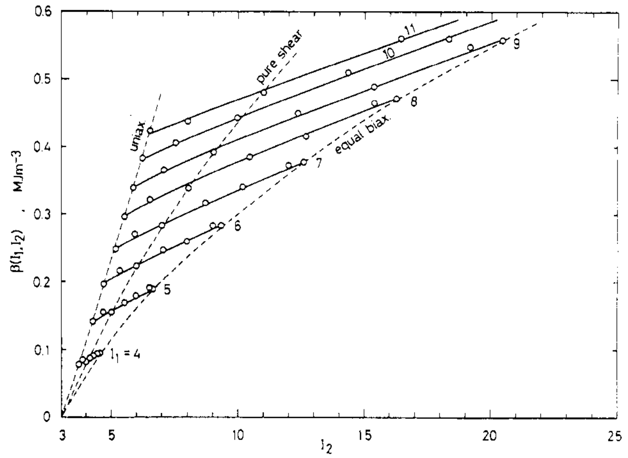

Figure 3. Plot of the energy function $\beta(I_1,I_2)$ against I_2 at constant I_1.

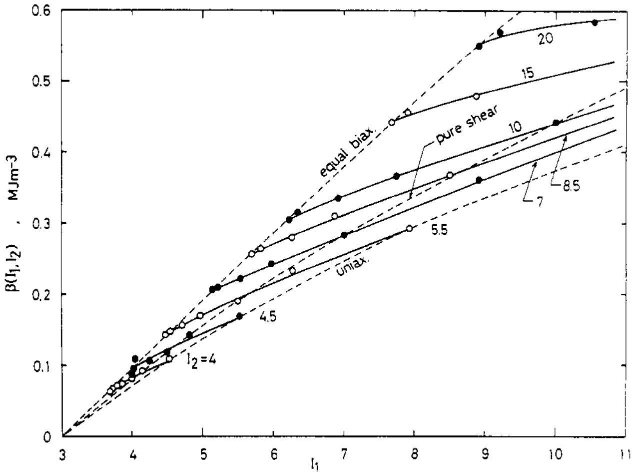

Figure 4. Plot of $\beta(I_1,I_2)$ against I_1 at constant I_2.

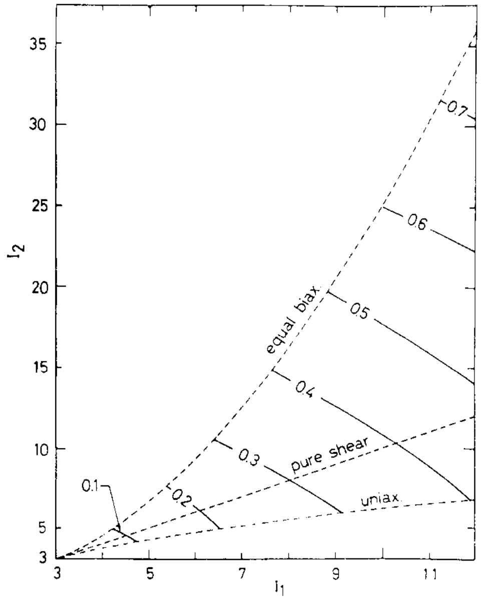

Figure 5. Contour diagram of $\beta(I_1,I_2)$, MJ m^{-3}, on the I_1–I_2 domain.

Table I

vulcanizates[a]	temp range, °C	stretch ratio range	f_e/f	f_e/f deformation dependence	ref
NR	0-60	2.0	0.15	constant	5-7
NR, IR	30-60	2.8	0.1-0.2	decrease with λ_1	12
NR	30-60	4.0	0.1-0.25	decrease with λ_1	11
NR	25-100	1.1-2.1	0.12	constant	9
NR	20-60	0.3-0.9	0.12	constant	8[b]
NR	10-60	1.2-3.1	0.18-0.27	decrease with λ_1	14

[a] NR = natural rubber; IR = isoprene rubber. [b] Measured by torsion.

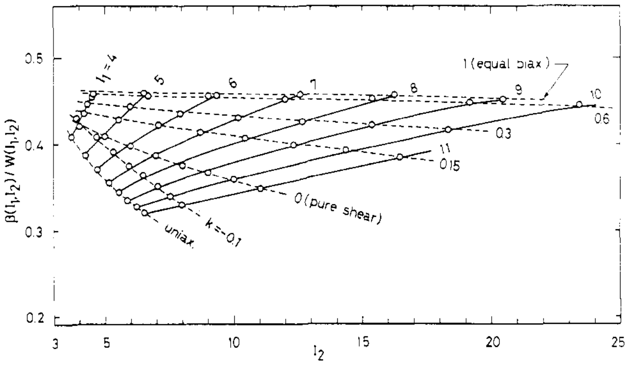

Figure 6. Deformation dependence of $\beta(I_1,I_2)/W(I_1,I_2)$ as a function of I_1 and I_2.

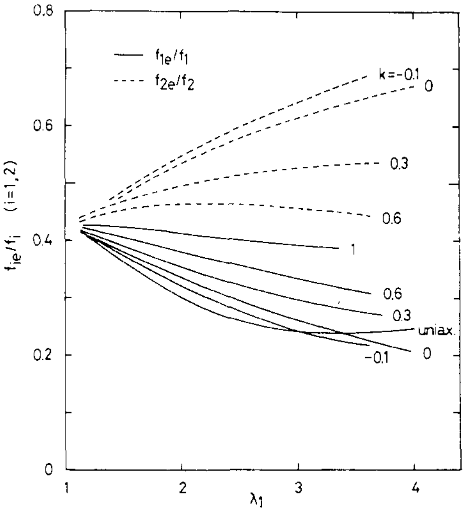

Figure 7. Relative magnitudes of the energetic component of force to the total force as a function of the principal stretch ratio λ_1 for several deformation modes.

As explained previously, the first term of eq 1 is considered to be the term related to the entropy change of the system and the second term to the internal energy change during deformation. It is interesting to examine the ratio of the energetic term (i.e., the second term) to the whole strain energy density W. The ratio $\beta(I_1,I_2)/W(I_1,I_2)$ is shown in Figure 6 for some typical deformation modes specified by k. The ratio decreases with increasing deformation and the rate of decrease is rapid in uniaxial deformation and slow in the equal biaxial deformation mode. The values of the ratio are in the range between 0.32 and 0.46 for this vulcanizate. As already shown, the function β is independent of temperature and the entropic term is proportional to temperature where the proportional coefficient C has already been obtained. Therefore, the temperature dependence of $\beta(I_1,I_2)/W(I_1,I_2)$ is easily estimated.

Discussion

Many researchers[5-21] have focused attention on the estimation of the internal energy change in the rubber network under isothermal conditions, mostly based on uniaxial extension data. These workers have separated the force component, which is considered to be caused by the effect of internal energy changes from the tensile force. The former force is called the energetic force component and is denoted by f_e. The contribution of f_e to the total extension force, f, is evaluated experimentally according to thermodynamic considerations. The typical technique employed in these investigations of the uniaxial extension of samples is the measurement of the extension force with varying temperature at constant volume V or constant pressure P under conditions of constant stretch ratio λ. The results reported to date are obtained almost entirely for uniaxial deformation. Our biaxial deformation experiment, under isothermal conditions, produces quantitatively the two components of the strain energy density function, an entropic component and an energetic component. As shown previously, the ratio $\beta(I_1,I_2)/W(I_1,I_2)$ lies between 0.32 and 0.46 at 293 K for all deformations. We may not be able to compare these data with other researchers' data because the deformation mode and experimental conditions employed for each case are different as are the materials used in each experiment. However, in our case, the value of f_e/f for uniaxial deformation can be estimated on the basis of the constitutive equations (20) and (21) for finite elastic deformation by means of the values of $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ as follows:

$$f_e/f = (f - f_s)/f \tag{19}$$

where

$$f = 2\left(\lambda - \frac{1}{\lambda^2}\right)\left(CT + \frac{\partial\beta}{\partial I_1} + \frac{1}{\lambda}\frac{\partial\beta}{\partial I_2}\right) \tag{20}$$

$$f_s = 2\left(\lambda - \frac{1}{\lambda^2}\right)CT \tag{21}$$

The values of $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ for uniaxial extension have already been estimated directly from the results of the biaxial experiment. In addition, the ratio f_{ie}/f_i ($i = 1, 2$) for biaxial deformation can be obtained in our case.

Some results from published f_e/f data[5-9,11,12,14] for natural rubber and isoprene rubber samples are collected in Table I together with the environmental conditions employed, including dependences of the ratio f_e/f on the stretch ratio. More precise consequences are reviewed by Mark[22] elsewhere. The results listed in Table I can be roughly divided into two groups. In one group,[5-10] f_e/f is almost independent of the stretch ratio in the moderate strain region but for the small-deformation region, f_e/f shows a dependence on the stretch ratio in which the value of f_e/f increases rapidly with decreasing deformation. In the other group,[11-21] the value of f_e/f decreases as the stretch ratio increases. These same trends of f_e/f with deformation have been reported for other polymer networks by many authors.[10,14-18]

In Figure 7, f_e/f from our data is plotted as a function of the stretch ratio at 293 K as well as f_{ie}/f_i for several biaxial deformations corresponding to $k = -0.1$, 0 (pure shear), 0.3, 0.6, and 1 (equal biaxial). f_{1e}/f_1 and f_{2e}/f_2 are plotted by solid and dashed lines in the figure. Of course, both curves coincide in the case of equal biaxial deformation. From Figure 7 it is seen that the ratio f_{1e}/f_1 decreases with increasing stretch ratio for all deformation modes. In uniaxial deformation, this decreasing tendency is most remarkable. On the other hand, the values of f_{2e}/f_2 for biaxial deformations are higher than those of f_{1e}/f_1 for all deformation modes examined here. Thus, the internal energy change shown by the function β contributes more to f_2 than to f_1. These tendencies can be understood if we consider the relations between the deformation dependence of $\beta(I_1,I_2)/W(I_1,I_2)$ and the constitutive equations of the finite elastic deformation shown in eq 1 and 2 in our previous paper. The values of f_e/f from our data for uniaxial deformation are similar to, but still somewhat higher than, those of the other researchers' data shown in Table I.

Shen[13] has shown that the values of f_e/f for real rubbers, whose strain energy density functions are represented by Mooney's equation[22] and Valanis and Landel's expression,[24] should decrease experimentally with increasing stretch ratio. He suggested that a part of the internal energy change might be attributable to intermolecular interactions. Kawabata[25] has suggested that $\partial W/\partial I_2$ is closely related to intermolecular forces on the basis of biaxial experiments of some vulcanizates, for which it has been shown in this paper that $\partial W/\partial I_2$ is equal to $\partial\beta/\partial I_2$.

Roe and Krigbaum[11,16] discussed the relation between the internal energy change and the Mooney constant C_2. They have found that the constant C_{2s}, which is the value obtained from the Mooney–Rivlin plot of the entropic force, f_s, separated from the total force f by a thermoelastic procedure, is smaller than the C_2 obtained from f. According to their results, the ratio C_{2s}/C_2 attains a value of almost 0.5 for natural rubber vulcanizate and nearly zero for a Viton elastomer, while the ratio C_{1s}/C_1 remains at about 0.9. It can be presumed that the internal energy change makes a larger contribution to C_2 than to C_1. This effect can be understood from the fact that the function β is related to Mooney's constant C_2 rather than C_1. At this point, it seems that their results agree with our experimental result.

On the other hand, Flory et al.[26-29] modified the equation of the classical theory of rubber elasticity in order to introduce the concept that the internal energy changes in the total free energy change of the network. They assumed that such energy originates essentially from an intramolecular source and the intermolecular interactions remain constant with deformation. Flory et al. tried to relate the quantity f_e/f to the molecular parameters by applying rotational isomeric state theory of chain configuration. However, the function β which we have found cannot be explained by their theory because the function β has been confirmed experimentally to be independent of temperature. In addition, it is concluded that f_e/f should be independent of deformation according to Flory's theory; however, the results of Shen[13] and Roe and Krigbaum[11,16] as well as our results of f_e/f show a clear dependence on deformation. Accordingly, we now believe much more strongly that the function β originates from intermolecular interactions such as intermolecular forces. In order to elucidate the molecular origin of the function β more clearly, extensive experiments, such as the dependence of the function β on cross-link density and on degree of swelling, will be needed.

Conclusion

The strain energy density function of isoprene rubber vulcanizate has been determined quantitatively by intergrating the principal stresses under biaxial extension using the experimental data presented in our previous paper.[1] The functional form of the strain energy density function derived in the previous paper is as follows:

$$W = CT(I_1 - 3) + \beta(I_1,I_2)$$

On the basis of this functional form, the magnitude of the function $\beta(I_1,I_2)$ has been determined as a function of I_1 and I_2, which are the first and second invariants of Green's deformation tensor. It has been found that the relative function β/W is between 0.32 and 0.46 for the entire deformation range examined in this experiment and that the value of β/W decreases with increasing deformation in the moderately large deformation region. As an example, in the case of pure shear, the relative value is 0.41 at $I_1 = I_2 = 5$ at 293 K and 0.36 at $I_1 = I_2 = 10$ at the same temperature. In order that our result can be compared with the mostly uniaxial extension results of other researchers, the ratio f_e/f is derived and is considered to be the proportion of the tensile force caused by the internal energy change accompanying the uniaxial extension. Both sets of results are nearly coincident.

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