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Dependence of Strain Energy Density Function on Cross-Link Density and Degree of Swelling for *cis*-1,4-Polyisoprene Rubber Vulcanizates

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ABSTRACT: The strain energy density function, W, of *cis*-1,4-polyisoprene rubber vulcanizates is measured by a biaxial extension experiment over the temperature range 0–80 °C in order to explain the dependence of the strain energy density function on the degree of cross-link density and the degree of swelling of the vulcanizate. In previous papers, the function W has been presented in a form consisting of two separate terms such that $W = CT(I_1 - 3) + \beta(I_1,I_2)$, where C is a constant and T is temperature (K). In this paper, it is confirmed that this functional form is valid for vulcanizates having various degrees of cross-link density and also for vulcanizates in various degrees of swollen states. A quantitative analysis based on the above result relates the dependence of the function β to the cross-link density and to the degree of swelling. It has been explained that, first, the cross-link density has a much greater effect on the magnitude of the function β than the effect on the first term and, second, the magnitude of the function β sharply decreases with increasing swelling even though the influence of the decrease of the effective number of network chains per unit volume caused by the swelling is subtracted. A discussion about the origin of the energy expressed by the function β is presented.

1. Introduction

In previous papers,[1,2] the functional form of the strain energy density of *cis*-1,4-polyisoprene rubber vulcanizate was investigated experimentally by means of biaxial extension at various temperatures, and the form shown by eq 1 was introduced:

$$W = CT(I_1 - 3) + \beta(I_1,I_2) \tag{1}$$

where C is a constant, T is temperature (K), I_1 and I_2 are, respectively, the first and second invariants of Green's deformation tensor, and β is a function of deformation only. The first term on the right-hand side of eq 1 corresponds to the energy derived by the classical theory of rubber elasticity, which is based on entropy elasticity. The second term on the right-hand side of eq 1 is a new term which has not been predicted by any theories of rubber elasticity. The function β is independent of temperature over the temperature range 0–80 °C, over which the samples are considered to be in the rubbery region; therefore, the energy term may originate from energy sources other than entropy elasticity. Also in our previous paper,[2] a quantitative analysis of the W function given by eq 1 was carried out based on the experimental data, and it was demonstrated that the magnitude of the β function is about 30–40% of that of the whole strain energy W in the deformation range studied.

The strain energy density W is substituted into a constitutive equation of an elastic and incompressible body in the two derivative forms, with $\partial W/\partial I_1$ and $\partial W/\partial I_2$ as material parameters. The function β also appears in the derivative forms as shown in eq 2:

$$\partial W/\partial I_1 = CT + \partial\beta/\partial I_1 \tag{2a}$$

$$\partial W/\partial I_2 = \partial\beta/\partial I_2 \tag{2b}$$

It is noted that $\partial W/\partial I_2$ consists of only a derivative of the β function. As has been pointed out in several papers,[3-7] the two material parameters $\partial W/\partial I_1$ and $\partial W/\partial I_2$ vary in magnitude in such a complex manner that these functions cannot simply be replaced by Mooney's constants.[8] The main reason for this complexity is considered to be that the function β has a direct effect upon both $\partial W/\partial I_1$ and $\partial W/\partial I_2$ as shown in eq 2, where $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ change upon deformation.

In this paper, two experimental results are presented for the *cis*-1,4-polyisoprene rubber vulcanizate. One of these experimental results is that the functional form of the strain energy density, which is separated into two terms as shown in eq 1, is still preserved even for the vulcanizate which has a different cross-link density and is in the swollen state. The other experimental result is the dependence of the function β on the cross-link density and on the degree of swelling. These experimental surveys have been carried out to explain as far as possible the origin of the strain energy expressed by the function β which appears in eq 1.

2. Experimental Section

The first part of the experiment is a survey of the dependence of the strain energy density function on the cross-link density of the vulcanizates. The dependence of the strain energy density function on the cross-link density is examined over a temperature range from 0 to 80 °C. The second part of the experiment is a survey of the effect of swelling on the strain energy density function, especially on the function β.

Four isoprene rubber vulcanizate samples were prepared as shown in Table I. The conditions of vulcanization are the same for all samples except the amount of sulfur. After roll mixing, the compounds were cured at 145 °C by a hot press for 30 min to obtain a sheet specimen of 1-mm thickness.

The effective number of network chains per unit volume, which is denoted by ν, for those samples is listed in Table II. The numbers shown in Table II were estimated from the measured value of the constant C in the first term on the right-hand side of eq 1 by using the relation $C = (1/2)\nu k$, where k is Boltzmann's constant, after the validity of the functional form of eq 1 had been confirmed for each of the samples. At the same time, the values of ν were estimated by two other methods as a means of reference. One set of values was obtained from Mooney's constant, C_1, which was evaluated by a Mooney–Rivlin plot[8] of uniaxial extension data and is denoted by ν_C. The other set of values was obtained from Flory's swelling theory[9] based on the statistical thermodynamics of swollen vulcanizate and is denoted by ν_F in Table II. A considerable difference is evident between the measured values obtained by the three methods and, of course, only the values of ν which were obtained from our biaxial experiment are consistent with the experimental results of our biaxial deformation. Therefore, the values ν from the biaxial deformation experiment will be used for the analyses in this paper.

Samples IR225, IR250, and IR275, shown in Table II, are preswollen vulcanizates prepared for the survey of the effect of swelling on the strain energy density function. During the preparation of these samples, *n*-hexadecane was added to the rubber together with vulcanizing agents before vulcanization,[10,11] and vulcanizates containing 25, 50, and 75 parts of *n*-hexadecane per 100 parts of rubber were prepared as shown in Table II. Sulfur content and other vulcanization conditions are exactly the same as those of sample IR2, which contains 2 parts of sulfur per 100

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Table I
Compositions of Samples[a]

	IR-2200	S, phr[b]	ZnO, phr	St acid, phr	SP, phr	MBTS, phr	TMTD, phr	*n*-hexadecane, phr
IR1	100	1	5	1	1	1	0.1	
IR2	100	2	5	1	1	1	0.1	
IR3	100	3	5	1	1	1	0.1	
IR5	100	5	5	1	1	1	0.1	
IR225	100	2	5	1	1	1	0.1	25
IR250	100	2	5	1	1	1	0.1	50
IR275	100	2	5	1	1	1	0.1	75

[a] Cure conditions: cure temperature, 145 °C; cure time, 30 min. [b] phr: parts per 100 parts of rubber by weight.

Table II
Effective Number of Chains (ν)

	S, phr	*n*-hexadecane, phr	V_r[a]	$10^5\nu$, mol/cm^3	$10^5\nu_C$,[b] mol/cm^3	$10^5\nu_F$,[c] mol/cm^3
IR1	1		1	8.47	7.30	10.95
IR2	2		1	9.61	9.21	12.66
IR3	3		1	11.10	11.17	14.36
IR5	5		1	13.50	13.86	17.78
IR225	2 (swollen)	25	0.858	8.64[d]		
IR250	2 (swollen)	50	0.705	7.45[d]		
IR275	2 (swollen)	75	0.617	6.61[d]		

[a] V_r = volume fraction of rubber in the swollen state. [b] $\nu_C = \nu$ estimated from Mooney's constant, C_1. [c] $\nu_F = \nu$ estimated from swelling measurement based on Flory's theory. [d] This value of ν shows the effective number of chains per unit volume of the vulcanizate in the unswollen state. The volume in the unswollen state was simply estimated by multiplying the volume of the swollen state by V_r.

parts of rubber. The densities of these swollen vulcanizates were measured by the density-gradient tube method in order to estimate the volume fraction of rubber in the swollen state, assuming conservation of mass. The volume fraction is expressed as the swelling ratio and denoted by V_r in this paper. Values of the V_r for the three swollen samples are shown in Table II. As mentioned before, these samples were cured under exactly the same conditions as for the reference sample IR2 except the content of the diluent. However, the values of the number of cross-links of these swollen samples referred to the volume in the unswollen state are not necessarily equal to each other because of the curing of the preswollen rubber. Therefore, the values of ν were estimated by eq 1 for each swollen sample after the confirmation of the validity of the separate form for *W* shown in eq 1 and also listed in Table II. It should be noted here that the expression "swelling" as used in this paper has a meaning somewhat different from its ordinary meaning. This expression usually refers to dilution of a network after cross-linking. The samples used here were prepared in such a manner that the network was diluted before cross-linking, and these samples are expressed here as swollen vulcanizate.[10,11]

The experimental method employed here is the biaxial stress relaxation method, which has already been described in the previous paper.[1] The isochronal data at 5 min were measured over a temperature range 0–80 °C at moderately large deformation such that the maximum principal stretch ratio was 2.5. The vulcanizates tested here almost attain their equilibrium state at about 5 min, and very little relaxation is observed after that time.[1,2] The stress–strain curves of all the samples used in this experiment do not show an upward curvature at high extension, as in a sigmoidal-shaped curve, which may be due to the non-Gaussian network chains in this limited deformation region. The apparatus used here and the method of data processing to obtain the derivatives of the strain energy density function are the same as reported in our previous papers.[1,2] That is, two methods have been applied to evaluate the strain energy density function *W*. One of these methods is to estimate $\partial W/\partial I_1$ and $\partial W/\partial I_2$ as function of I_1 and I_2 from the constitutive equation based on the data of stress–strain relations obtained from various biaxial deformations. The other method is to measure the magnitude of *W* by integration of the stresses as the energy required for deforming the body from the undeformed state to the deformed state. Both methods will be applied in this paper.

3. Results

Effect of Cross-Link Density. The 5-min isochronal values of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ measured at 20 °C are shown in Figure 1 as a function of I_1 and I_2 for the four samples having different cross-link densities. It is shown in this figure that the functional forms of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for these samples are similar to each other, but their magni-

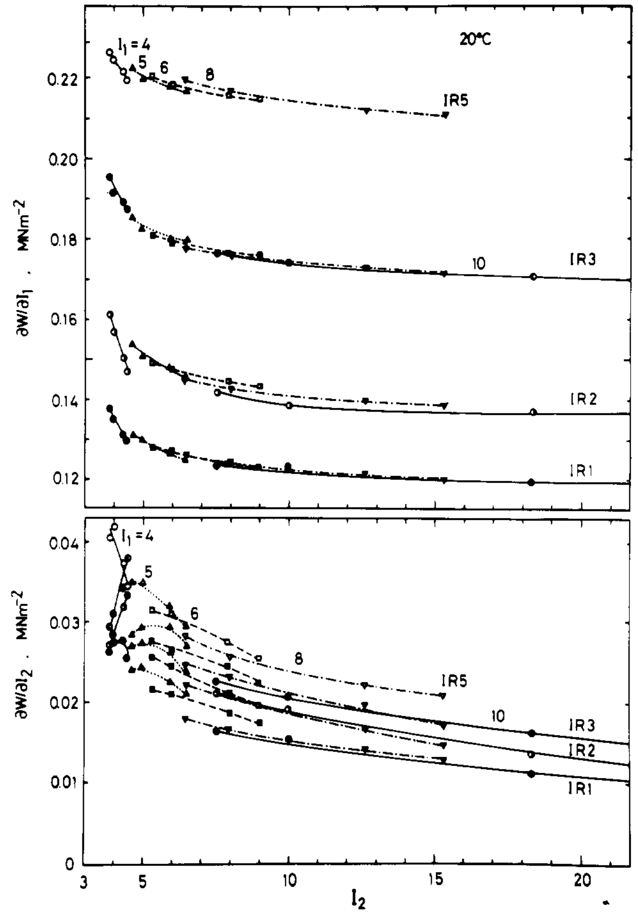

Figure 1. $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for samples having different cross-link densities (5-min isochronal data are shown).

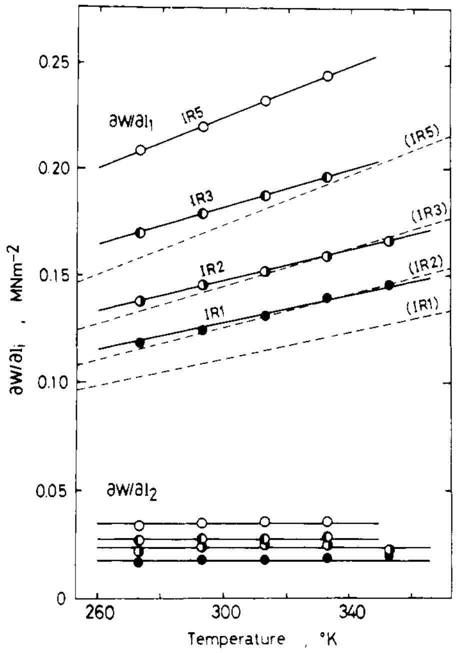

Figure 2. Temperature dependence of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ under the deformation $I_1 = I_2 = 7$ for samples having different cross-link densities (solid lines). Broken lines are drawn in such a manner that the lines go through $T = 0$ K on the abscissa and are parallel to the $\partial W/\partial I_1$ line for each of the samples.

tudes are clearly dependent on cross-link density. Similar results were obtained at different temperatures over the region from 0 to 80 °C.

Figure 2 shows the temperature dependence of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for the deformation $I_1 = I_2 = 7.0$ (pure shear) for these four specimens. First, as can be seen from Figure 2, the values of $\partial W/\partial I_1$ for these samples increase with the degree of cross-link density and also increase linearly with temperature over the temperature range studied. However, every linear relation between $\partial W/\partial I_1$ and T does not tend to 0 K on the abscissa. The slopes of these $\partial W/\partial I_1$–T relations are independent of deformation for every sample. As shown in our previous paper,[1] this common-slope relation of $\partial W/\partial I_1$ implies that the expression of W by two separate terms as in eq 1 is valid for the other samples used in this experiment having different cross-link densities. As discussed in our previous paper,[1] the first term on the right-hand side of eq 1 may be considered to be the energy derived from the entropy elasticity.[2] On the basis of this assumption, the number of effective chains, ν, shown in Table II have been obtained from the observed values of the first term on the right-hand side of eq 1 by the method described in our previous paper.[1]

Figure 2 also shows that $\partial W/\partial I_2$ is almost independent of temperature over the temperature range examined and that the values of $\partial W/\partial I_2$ for the four specimens increase with increasing cross-link density. Following the method shown in our previous paper,[1] the functions $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ have been measured for each of the samples and are shown in Figure 3. Both the $\partial\beta/\partial I_1$ and the $\partial\beta/\partial I_2$ are clearly dependent on cross-link density. Figure 4 shows that at 20 °C both derivatives increase with increasing ν over the whole deformation region examined. In order to examine the dependence of β on ν directly, the magnitude of the function β was evaluated from the stress–strain relation under biaxial extension using the integration method reported in the previous paper.[2] The result is shown in Figure 5 as a function of ν for each of the samples at 20 °C under several pure-shear deformations. It is observed from this figure that the function β is nonlinearly dependent on ν. Figure 6 shows the dependence of β on ν by normalizing those values to a reference sample, IR2. Two dot–dash lines correspond to the cases where β is proportional to ν or to ν^2. The plotted data are approximately scattered between these two lines and lie approximately on the line $\nu^{1.5}$. The strain energy density function shown in eq 1 may be expressed by eq 3 and, approximately, by eq 4, where the effect of ν on β is separated as a front factor.

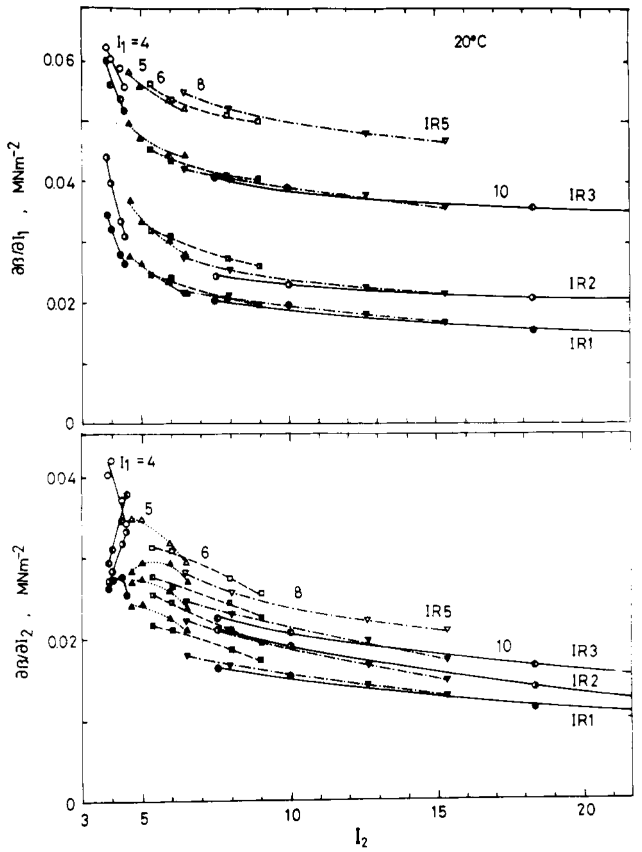

Figure 3. $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ derived from the $\partial W/\partial I_i$ for samples having different cross-link densities.

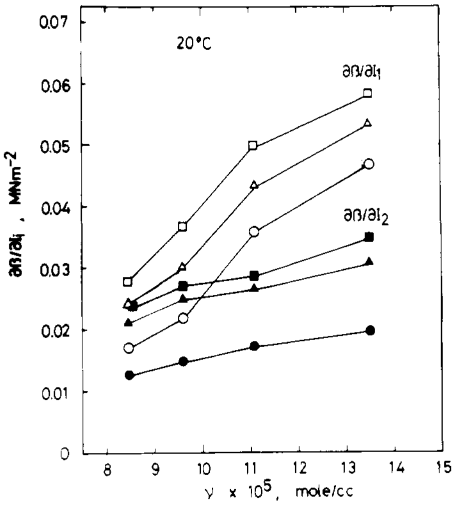

Figure 4. Dependence of $\partial\beta/\partial I_i$ on ν under several deformations at 20 °C: (□,■) $I_1 = 5, I_2 = 4.7$; (△,▲) $I_1 = I_2 = 5$; (○,●) $I_1 = 8, I_2 = 15.8$.

$$W = \tfrac{1}{2}\nu kT(I_1 - 3) + \beta(\nu,I_1,I_2) \tag{3}$$

$$W = \tfrac{1}{2}\nu kT(I_1 - 3) + \nu^{1.5}(1/\nu_0^{1.5})\beta_0(I_1,I_2) \tag{4}$$

where ν_0 and β_0 are the effective number of chains per unit

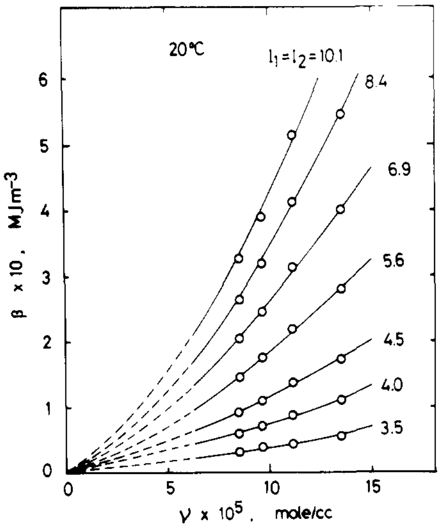

Figure 5. Dependence of the magnitude of β on ν under several deformations at 20 °C.

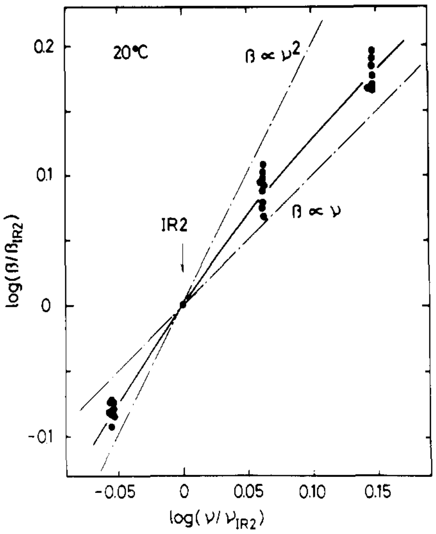

Figure 6. Relative values of the function β referred to IR2 at 20 °C. The data in Figure 5 are replotted on this figure. An estimated relation is $\beta \propto \nu^{1.5}$.

volume and the function β of the reference sample IR2, respectively. It is interesting to note that the second term on the right-hand side of eq 4 depends on ν more strongly than does the first term. In eq 4, the effect of ν on the function β is approximated by a separate form based on the experimental result; however, the result shown in Figure 4 suggests that the dependence is not as simple as shown in eq 4 but rather is more complicated, and the function β should, strictly speaking, be expressed as a function of ν as shown in eq 3.

Strain Energy Density Function of Swollen Vulcanizate. For the purpose of revealing the energy source of the function β, which has not been interpreted from molecular theory, a survey of the strain energy density function of swollen vulcanizates seems to be important. The same experiment and data processing were carried out for three swollen samples, IR225, IR250, and IR275, each of which contains a different amount of diluent as shown in Table II. Figure 7 shows the functional forms of $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for the three swollen samples and an unswollen sample, IR2, as a reference. The validity of the separate form for W shown in eq 1 has again been confirmed for the function W of these swollen samples over a temperature range from 20 to 60 °C. $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ of these samples are derived by the analysis of the temperature dependence of $\partial W/\partial I_i$. It should be noted here that the strain energy density of the swollen system should be reduced in magnitude because of the reduction in the effective number of chains by volume dilatation due to swelling. Simply, the following equation is obtained:

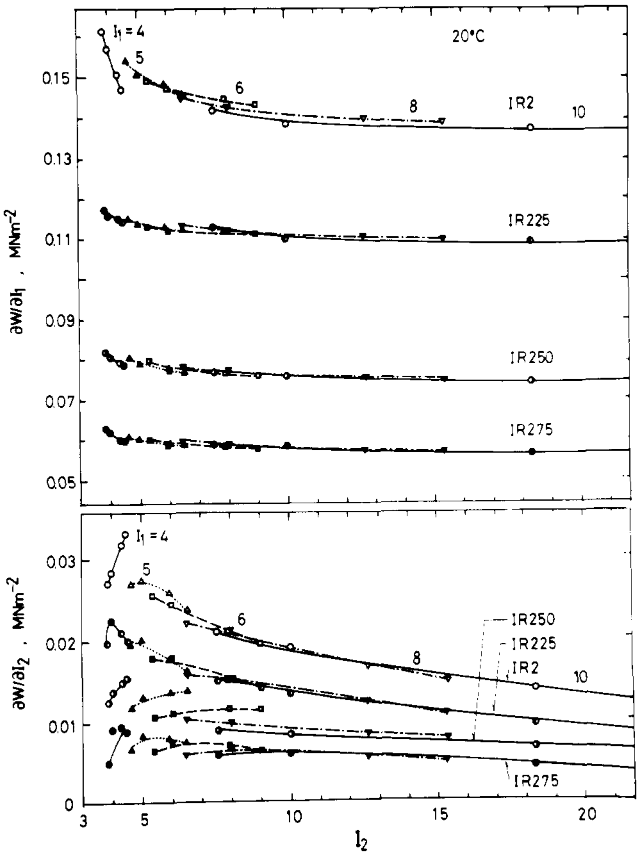

Figure 7. $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for three samples in different swollen-state degrees at 20 °C (5-min isochronal data). IR2 is the unswollen-state reference sample.

$$W = V_r\tilde{W} = V_r[{}^1\!/_2\tilde{\nu}kT(I_1 - 3) + \tilde{\beta}(I_1,I_2,\tilde{\nu},V_r)] \qquad (5)$$

where the tilde indicates the value measured by the unit volume in the unswollen state. $\tilde{\nu}$ and the $\tilde{\beta}$ are defined by $\tilde{\nu} = \nu/V_r$ and $\tilde{\beta} = \beta/V_r$. The $\tilde{\nu}$ values of these three swollen vulcanizates are not actually the same, as seen in Table II, because of the difference in the actual vulcanizing process of these three preswollen rubbers. In order to eliminate the effect of the variation of $\tilde{\nu}$ on $\tilde{\beta}$ and to see the effect of V_r clearly, the relation with respect to the effect of ν on β in eq 4 may be applied to $\tilde{\beta}$ in eq 5. A function $\tilde{\beta}_0(I_1,I_2,V_r)$ is defined here to eliminate the effect of $\tilde{\nu}$ from $\tilde{\beta}$ such that

$$\tilde{\beta}_0(I_1,I_2,V_r) = \tilde{\beta}(I_1,I_2,\tilde{\nu},V_r)/(\tilde{\nu}/\nu_0)^{1.5} \qquad (6)$$

The functions $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ of these swollen samples are shown in Figure 8. The effect of the decrease of chain density due to swelling on strain energy density has been canceled out in these derivatives; however, the derivative functions are still dependent on V_r and their values decrease with increasing swelling as seen in Figure 8. In order to show clearly the effect of swelling on the function $\tilde{\beta}$, the functions $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ are shown as function of V_r in Figure 9, where the difference in the $\tilde{\nu}$ values for each of these samples was equalized by using $\tilde{\beta}_0$ instead of $\tilde{\beta}$. As seen from Figure 9, both the functions $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ decrease with increasing swelling. On the other hand, the relative $\tilde{\beta}_0$ values referred to $\beta_0(I_1,I_2)$ are shown in Figure 10, where the value of the $\tilde{\beta}_0$ was obtained by the integration method.

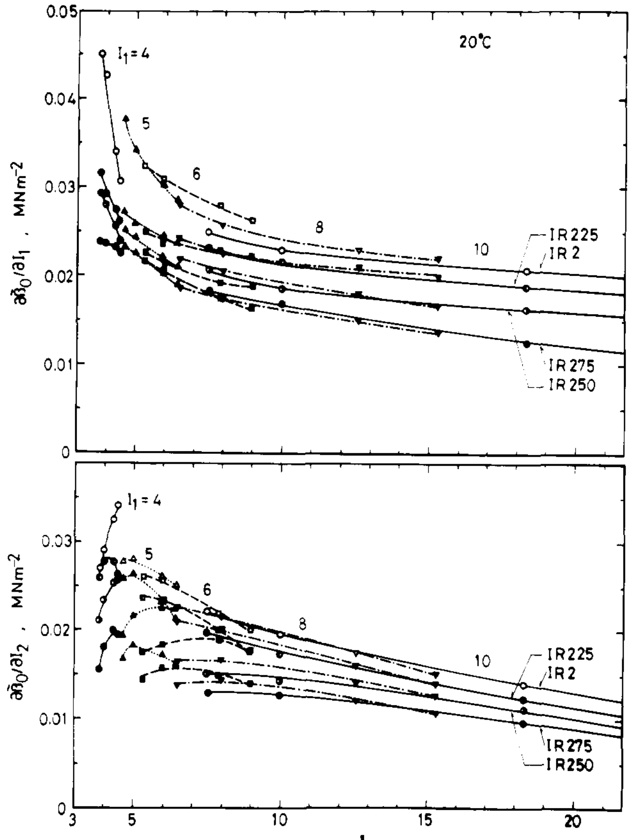

Figure 8. $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ for samples with different degrees of swelling at 20 °C (5-min isochronal data). IR2 is the unswollen-state reference sample.

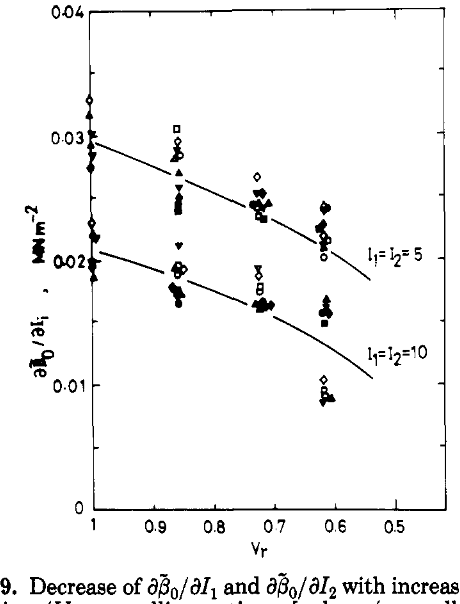

Figure 9. Decrease of $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ with increasing degree of swelling (V_r = swelling ratio ≡ [volume(unswollen)]/[volume(swollen)]: (▽) 20 °C; (△) 30 °C; (○) 40 °C; (□) 50 °C; (◇) 60 °C. $\partial\tilde{\beta}_0/\partial I_1$ is shown by open symbols and $\partial\tilde{\beta}_0/\partial I_2$ by closed symbols.

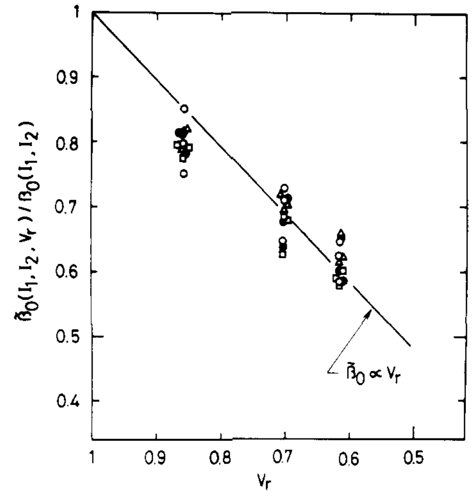

Figure 10. Relative value of the function $\tilde{\beta}_0$ over the temperature range 20–60 °C referred to the value at V_r = 1 (unswollen state): (○) $I_1 = I_2 = 10$; (△) $I_1 = I_2 = 7$; (▲) $I_1 = I_2 = 5.5$; (□) $I_1 = I_2 = 4$.

The steep decrease in the value of $\tilde{\beta}_0$ with increasing swelling can be observed in this figure. It is noted that a common curve for this decrease is observed for various deformations and at various temperatures and that the line goes through 1 of the relative value at V_r = 1. The slope of this decreasing curve is, however, a little higher than those of $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$. Also, strictly speaking, there is a difference between the slopes of $\partial\tilde{\beta}_0/\partial I_1$ and $\partial\tilde{\beta}_0/\partial I_2$ as seen in Figure 9. These differences may be caused by the fact that the dependence of the function $\tilde{\beta}_0$ on V_r is not so simple and its complexity is magnified in its derivative forms.

One approximation for the function $\tilde{\beta}$ is obtained from the result shown in Figure 10 such that

$$\tilde{\beta}(I_1,I_2,V_r) = V_r\tilde{\beta}_0(I_1,I_2) \qquad (7)$$

4. Discussion

The source of the energy density expressed by the function $\tilde{\beta}$ is still undefined. However, the validity of the functional form of the strain energy density, which consists of two separate terms as shown in eq 1, has been proved experimentally for the various samples used in this experiment under various conditions. The experimental results imply that the function $\tilde{\beta}$ is still independent of temperature, regardless of the degree of cross-link density and the degree of swelling. In addition, the results shown by eq 4 and 7 suggest more clearly that the first and second terms on the right-hand side of eq 1 originate from different energy sources because of their different dependence on cross-link density and swelling. One of the distinctive results is that the function $\tilde{\beta}$ decreases in value remarkably with increasing swelling. The proportion of the magnitude of $\tilde{\beta}$ to that of W is estimated in Table III for several different values of ν and V_r based on the experimental results reported here. The ratio $\tilde{\beta}/W$ decreases remarkably with increasing swelling. Kawabata[7] has reported the possibility that $\partial W/\partial I_2$ may be closely related to intermolecular forces based on the analysis of a simple network model. It is noted that $\partial W/\partial I_2$ is related only to the energy $\tilde{\beta}$ as shown in eq 1. If Kawabata's presumption is valid and the swelling decreases the intermolecular forces, then the results obtained in the swelling experiment would follow logically.

The effect of cross-link density on the second term on the right-hand side of eq 1, that is, the function $\tilde{\beta}$, is much stronger than its effect on the first term, which is considered to be the term related to entropy elasticity. The explanation of these effects is still undefined at this stage. It can be estimated that the intermolecular force is relatively sensitive to cross-link density. Another possibility to be considered is that the entanglement of the molecular chains decreases with increasing swelling as reported in some papers.[12-16] The decrease in the entanglement may change the apparent cross-link density. However, as mentioned above, the effect of this cross-link density on

Table III
Comparison between the Magnitudes of β and W at 20 °C

	$10^5\nu$, mol/cm^3	V_r		I_1 ($=I_2$; pure shear)			
				4.55	6.05	7.91	10.11
IR1	8.47	1	W	0.258[b]	0.489	0.764	1.080
			β	0.095	0.169	0.248	0.332
			β/W	0.369	0.345	0.324	0.308
IR2	9.61	1	W	0.298	0.567	0.886	1.247
			β	0.113	0.203	0.300	0.398
			β/W	0.379	0.358	0.338	0.319
IR3	11.10	1	W	0.354	0.676	1.061	1.504
			β	0.140	0.256	0.384	0.523
			β/W	0.396	0.378	0.362	0.347
IR5	13.50	1	W	0.436	0.835	1.320	
			β	0.176	0.324	0.497	
			β/W	0.404	0.388	0.377	
IR225	8.64[a]	0.858	W	0.227	0.439	0.691	0.982
			β	0.074	0.136	0.204	0.275
			β/W	0.323	0.310	0.295	0.280
			$\tilde{\beta}$	0.090	0.166	0.249	0.337
IR250	7.45[a]	0.705	W	0.144	0.282	0.447	0.638
			β	0.039	0.075	0.114	0.154
			β/W	0.271	0.267	0.254	0.242
			$\tilde{\beta}$	0.078	0.150	0.227	0.307
IR275	6.61[a]	0.617	W	0.105	0.205	0.327	0.469
			β	0.023	0.044	0.067	0.092
			β/W	0.221	0.214	0.204	0.196
			$\tilde{\beta}$	0.064	0.121	0.183	0.252

[a] $\tilde{\nu}$. [b] In MJ m^{-3}.

the function β is much higher than its effect on the first term. Therefore, there is a possibility that the decrease of the entanglement may rapidly decrease the β function. Even though the number of trapped entanglements should not change on swelling, there is a possibility that the function may decrease its value with swelling on the basis of a network theory analyzed by Graessely and Pearson.[21] Some experimental work[17-20] has indicated that Mooney's constant, C_1, is not affected by swelling and that only C_2 decreases with swelling. C_1 is the estimated value of $\partial W/\partial I_1$ and C_2 is the estimated value of $\partial W/\partial I_2$. Our experimental results show that $\partial W/\partial I_2$ (that is, $\partial\beta/\partial I_2$) is dependent on the swelling, but $\partial W/\partial I_1$ is also dependent on the swelling. The disagreement between the uniaxial and the biaxial extension data may be caused by the technique used for obtaining C_1 and C_2 by the Mooney–Rivlin plot of uniaxial extension data. $\partial W/\partial I_1$ and the $\partial W/\partial I_2$ do not always coincide with C_1 and C_2, respectively, when both $\partial W/\partial I_1$ and $\partial W/\partial I_2$ change with deformation. As shown before, the dependence of the form of the function β on both cross-link density and swelling ratio is not so simple. The dependence of the function β and that of its derivatives $\partial\beta/\partial I_1$ and $\partial\beta/\partial I_2$ on, for example, the degree of cross-link density are not exactly identical. However, an estimated equation which is useful for examining the influence of ν and V_r on the strain energy density function is as follows. By substituting the relation shown in eq 7 into eq 5, we obtain

$$W = \tfrac{1}{2}V_r\tilde{\nu}kT(I_1 - 3) + (\tilde{\nu}/\nu_0)^{1.5}V_r^{\,2}\beta_0(I_1,I_2) \qquad (8)$$

5. Conclusion

The strain energy density function for *cis*-1,4-polyisoprene rubber vulcanizate was investigated with respect to its dependence on the cross-link density and the degree of swelling by means of biaxial extension experiments. It has been demonstrated that the form of the strain energy densty function, which consists of two separate terms as already formulated in the previous paper, is valid for these vulcanizates having different cross-link densities and different degrees of swelling. The forms of the function W for these vulcanizates have been explained and presented as the following equation:

$$W = \tfrac{1}{2}\nu kT(I_1 - 3) + \beta(I_1,I_2,\nu,V_r) \qquad (9)$$

As an approximate equation, the following form of the strain energy density function has been proposed:

$$W = V_r[\tfrac{1}{2}\tilde{\nu}kT(I_1 - 3) + (\tilde{\nu}/\nu_0)^{1.5}V_r\beta_0(I_1,I_2)] \qquad (10)$$

The distinct features of this equation are that cross-link density has a remarkable effect on the magnitude of the function β and that the magnitude of β decreases with increasing degree of swelling. The explanation for this behavior of vulcanizates is still undefined; however, the results obtained in this paper and those reported earlier[1,2] will provide a strong base for future research on rubber elasticity.

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