

# Large Deformation Tensile Properties of Elastomers.

## I. Temperature Dependence of $C_1$ and $C_2$ in the Mooney-Rivlin Equation

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### Synopsis

Tensile stress-strain data were determined at various extension rates and temperatures on unfilled butyl and silicone vulcanizates and on six hydrofluorocarbon (Viton A-HV) vulcanizates that contain between 0.90 and  $12.2 \times 10^{-6}$  mole of effective network chains per unit volume of gel rubber. From 1-min. isochronal data, values of  $C_1$  and  $C_2$  in the Mooney-Rivlin equation were derived. For the butyl and silicone vulcanizates from, respectively,  $-20$  to  $150^\circ\text{C.}$  and  $-45$  to  $200^\circ\text{C.}$ ,  $C_1$  increases with temperature at a rate which is in reasonable agreement with published data from force-temperature measurements. Because  $C_2$  is sensibly temperature independent over these extended temperature ranges, it is concluded that  $C_2$  is a finite quantity under equilibrium conditions. Time-dependent behavior was observed on the Viton A-HV vulcanizates between  $-5$  and  $230^\circ\text{C.}$  For each vulcanizate between about  $25$  and  $230^\circ\text{C.}$ ,  $C_1 273/T$  is temperature independent, but it increases with decreasing temperature below about  $25^\circ\text{C.}$  Except at the lowest temperatures,  $C_2 273/T$  decreases with increasing temperature, the rate of decrease becoming progressively less with an increase in crosslink density. Above  $25^\circ\text{C.}$  the ratio  $C_2/C_1$ , which ranges from about  $90$  to  $0.6$ , decreases with an increase in either temperature or crosslink density. The time-dependent behavior of  $C_2 273/T$  appears to arise primarily from molecular processes whose relaxation times are considerably longer than the terminal relaxation time of individual chains.

### Introduction

The statistical theory of rubberlike elasticity<sup>1</sup> predicts that equilibrium stress-strain data from uniaxial tests in either tension or compression should obey the equation

$$\sigma = \frac{\nu_e}{V} \frac{\langle r^2 \rangle_i}{\langle r^2 \rangle_0} RT(\lambda - \lambda^{-2}) \quad (1)$$

where  $\sigma$  is the stress based on the cross-sectional area of the undeformed specimen,  $\lambda$  is the extension ratio,  $\nu_e/V$  is the moles of effective network chains in a volume  $V$ ,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\langle r^2 \rangle_i$  is the mean-square end-to-end distance of network chains at  $\lambda = 1$  and temperature  $T$ , and  $\langle r^2 \rangle_0$  is the same quantity for the chains when free of network constraints at the same temperature. Because in uniaxial tension

$\sigma$  normally increases less rapidly with  $\lambda$  than predicted by eq. (1), such data are commonly represented by the Mooney-Rivlin<sup>2,3</sup> equation:

$$\sigma/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2/\lambda \quad (2)$$

where  $C_1$  and  $C_2$  are constants. This equation usually represents tensile data reasonably well for values of  $\lambda$  between about 1.2 and 2 or 3. At larger deformations, the stress increases more rapidly than predicted by eq. (2) because of the finite extensibility of the network chains.

In contrast to behavior in tension, uniaxial compression data appear to fit eq. (1) quite well. Rivlin and Saunders<sup>4</sup> found that data from tests in uniform two-dimensional extensions (a test equivalent to uniaxial compression) gave a value of  $\sigma/(\lambda - \lambda^{-2})$ , which varied by about  $\pm 5\%$  over the range  $0.08 < \lambda < 0.5$ . Using an apparatus specially designed to give a uniform deformation in uniaxial compression, Foster<sup>5</sup> obtained data at values of  $\lambda$  between 0.68 and 0.98 and found that they conformed very closely to eq. (1). Wood<sup>6</sup> found that data obtained in both tension and compression by various investigators could be represented over the range  $0.5 < \lambda < 3.5$  by the empirical equation of Martin, Roth, and Stiehler.<sup>7</sup> From considerations of the data in terms of this and other equations, Wood<sup>6</sup> concluded that: (1) data in the range  $0.5 < \lambda < 1$  deviate from eq. (1) by less than 4%; and (2) data at low tensile elongations cannot even be represented by the Mooney-Rivlin equation; i.e., over some range of  $\lambda$  in the vicinity of unity,  $C_2$  apparently decreases and becomes essentially equal to zero in uniaxial compression.

The available data are consistent with Rivlin's<sup>3</sup> finite deformation theory which gives for the uniaxial behavior (in either tension or compression) of an incompressible material

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = (\partial W/\partial I_1) + \frac{1}{\lambda} (\partial W/\partial I_2) \quad (3)$$

where  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$  are derivatives of the stored energy function with respect to the strain invariants  $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$  and  $I_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$ ; the  $\lambda$ 's are the extension ratios in the three mutually perpendicular directions. Extensive data of Rivlin and Saunders,<sup>4</sup> obtained from different types of biaxial tensile tests on natural rubber vulcanizates at ambient temperature, suggest that  $\partial W/\partial I_1$  is a constant and that  $\partial W/\partial I_2$  decreases with an increase in  $I_2$ . When the resulting values of  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$  were substituted in eq. (3), they<sup>4</sup> found that their uniaxial data in *both* tension and compression were represented quite precisely. These results show that  $C_1$  and  $C_2$ , obtained by fitting tensile data to eq. (2), are not the same as  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$ , because uniaxial compression data give  $C_2 \cong 0$  and tensile data give a positive value for  $C_2$ . A qualitative explanation<sup>4</sup> follows: For a uniaxial test,  $I_2 = 2\lambda + \lambda^{-2}$  where  $\lambda$  is the extension ratio in the direction which is parallel to the applied force. The invariant  $I_2$  increases either as  $\lambda$  decreases in a compression test or as  $\lambda$  increases in a tensile test. In compression,  $(1/\lambda)\partial W/\partial I_2$  is essentially a

constant, because  $\lambda^{-1}$  increases by an amount sufficient to offset the decrease in  $\partial W/\partial I_2$ . In tension, however, both  $\lambda^{-1}$  and  $\partial W/\partial I_2$  decrease and these changes are such that  $(1/\lambda)\partial W/\partial I_2$  decreases in an almost linear fashion with  $\lambda^{-1}$ .

Because neither  $C_2$  nor  $\partial W/\partial I_2$  is predicted by the statistical theory, various explanations for the existence of these terms have been proposed, Ciferri and Flory<sup>8</sup> suggested that  $C_2$  reflects in large measure nonequilibrium effects. In recognition of this possibility, Ciferri and Hermans<sup>9</sup> considered a simple model containing a non-Newtonian viscosity element which causes the relaxation rate to decrease with a decrease in elongation. Using selected values of parameters for the model, they computed stress-strain data which conform to the Mooney-Rivlin equation.

Roe and Krigbaum<sup>10</sup> have reported that  $C_2$  for a natural rubber vulcanizate increases by 5% when the temperature is increased from 30 to 60°C. and that changes in internal energy affect  $C_2$  more than  $C_1$ . Although they were unable to explain the results quantitatively in terms of a cubic lattice model (Krigbaum and Kaneko<sup>11</sup>), which takes into account energy changes from intramolecular rotations, they conclude that such energy changes are important and that  $C_2$  will not vanish under equilibrium conditions.

DiMarzio<sup>12</sup> considered an elongation-dependent entropy of packing and was able to explain a portion of the usual deviation from eq. (1). Thomas<sup>13</sup> assumed that the free energy of a chain contains a term which is inversely proportional to the distance between chain ends. Although the resulting stored energy function agreed with experimental observations, Thomas did not postulate a reason for the additional term in the free energy expression.

Many rubber vulcanizates exhibit a slow relaxation process characterized by relaxation times which are markedly greater than the terminal (longest) relaxation time of individual network chains. For example, with decreasing frequency, the loss tangent of natural rubber vulcanizates decreases at a progressively slower rate and remains finite over an extended frequency range.<sup>14</sup> At low frequencies, the loss tangent increases with an increase in the molecular weight of network chains. Because of the slow relaxation process, whose molecular origin has not been established, it is often difficult to obtain equilibrium in stress relaxation, creep, and other types of mechanical tests. As a result, there has been considerable question about the extent to which the time-dependent processes affect  $C_2$ . Further, few studies have been made to delineate clearly the time and temperature dependence of  $C_2$  and the dependence of  $C_2$  on molecular parameters.

The influence of molecular parameters on  $C_2$  has been studied by Kraus and Moczygemba,<sup>15</sup> who prepared sulfur vulcanizates from polybutadiene polymers whose primary molecular weights varied from about  $8 \times 10^4$  to  $29 \times 10^4$ . Their data show that  $C_2$  increases with either primary molecular weight or crosslink density but that  $C_2/C_1$  decreases with an increase in crosslink density at a given primary molecular weight. (The

latter behavior is qualitatively similar to the dependence<sup>14</sup> of the low-frequency loss tangent on crosslink density.) They also prepared elastomers by curing a carboxy-terminated polybutadiene, having a molecular weight of about 5500, with a hexafunctional compound. These elastomers, which are believed to have few entanglement crosslinks, gave  $C_2 \cong 0$ . From the results, they<sup>15</sup> concluded that  $C_2$  for conventional vulcanizates may result from a slow relaxation process associated with the slippage of entanglement crosslinks. In this paper, a discussion is given of the temperature dependence of  $C_1$  and  $C_2$  derived from isochronal data obtained on several types of vulcanizates over extended temperature ranges. The purposes are: (1) to provide additional evidence that  $C_2$  for certain vulcanizates is not zero under equilibrium conditions; and (2) to show that the slow relaxation processes, which for certain vulcanizates persist over extended ranges of time and temperature at elevated temperatures, are reflected in a temperature-dependent  $C_2$ , whereas  $C_1$  remains sensibly constant.

### Materials and Experimental Methods

Unfilled vulcanizates of butyl, silicone [poly(dimethyl siloxane)], and hydrofluorocarbon rubbers were supplied by the Air Force Materials Laboratory at Wright-Patterson Air Force Base. The compounding formulas and cure conditions for the butyl and silicone vulcanizates are given elsewhere.<sup>16</sup> The butyl vulcanizate was sulfur-cured and contained 2.5 parts of zinc oxide per 100 parts of rubber. The silicone vulcanizate was cured with benzoyl peroxide and contained 5 parts of Cab-O-Sil (silica). Six hydrofluorocarbon vulcanizates, having different crosslink densities, were prepared from Viton A-HV gum stock, a copolymer of hexafluoropropylene and vinylidene fluoride (manufactured by E. I. du Pont de Nemours and Co.), which reportedly has a number-average molecular weight of about  $2 \times 10^5$ . The vulcanizates, designated by the symbols A-1, A-2, etc., contained 5 parts of MgO (Maglite Y), and the following parts of the crosslinking agent Diak No. 3 (*N,N'*-dicinnamylidene-1,6-hexanediamine): A-1, 0.2; A-2, 0.4; A-3, 0.6; A-4, 0.8; A-5, 1.0; and A-6, 2.0.

Table I gives characteristics of the vulcanizates. The data were obtained by the methods described in the notes beneath the table. Values of  $\nu_e/V_g$ , the moles of effective network chains per unit volume of gel rubber, were computed from  $C_1$  data (obtained as described subsequently) even though this method is somewhat questionable. However, derivation of  $\nu_e/V_g$  from either equilibrium swelling or equilibrium modulus data is likewise questionable. In support of the use of  $C_1$ , it can be stated that values of  $C_1$  for the Viton vulcanizates could be correlated quite well with the observed equilibrium swelling in acetone; also the obtained values of  $\nu_e/V_g$  increase essentially in direct proportion to the amount of curing agent used.

The small gel fraction and the few active chains in A-1 might suggest that a three-dimensional elastic network was not formed during vulcanization. That such a network was indeed formed is shown by two ob-

TABLE I  
 Characteristics of Vulcanizates

Vulcan- izate	2C <sub>1</sub> 273/T		gel		M <sub>c</sub> <sup>c</sup> × 10 <sup>-4</sup>	T <sub>g</sub> <sup>d</sup> °C.	Density at 20°C., g./ml.
	psi	dynes/cm. <sup>2</sup> × 10 <sup>-6</sup>	fraction, <sup>a</sup> g	(ν <sub>e</sub> /V <sub>g</sub> ) <sup>b</sup> × 10 <sup>5</sup>			
Silicone	11.8	0.814	0.89	4.03	—	-123°	1.000
Butyl	30.4	2.10	0.95	9.74	—	-68	0.949
Viton A-HV							
A-1	1.5	0.103	0.51	0.90	6.82	-29	1.844
A-2	5.5	0.38	0.70	2.39	4.40	-29	1.843
A-3	9.4	0.65	0.82	3.50	3.48	-29	1.842
A-4	16.0	1.10	0.90	5.41	2.55	-28	1.842
A-5	20.2	1.39	0.925	6.65	2.18	-28	1.841
A-6	38.8	2.68	0.964	12.2	1.31	-23.5	1.831

<sup>a</sup> The fraction of gel rubber in the silicone and butyl vulcanizates was determined by extracting specimens with benzene at its normal boiling point in a Soxhlet extractor for four days. Data on the Viton A-HV vulcanizates were obtained from the amount of soluble material extracted during the determination of equilibrium swelling in acetone. Because all soluble material probably was not removed, especially from A-1 and A-2, the gel fractions given in the table represent upper limits.

<sup>b</sup> ν<sub>e</sub>/V<sub>g</sub> is the moles of effective network chains per unit volume of gel rubber and was obtained from the equation (ν<sub>e</sub>/V<sub>g</sub>) = 2C<sub>1</sub>/gRT.

<sup>c</sup> Molecular weight of active chains estimated from equation M<sub>c</sub> = ρ/[(ν<sub>e</sub>/V<sub>g</sub>) + 2P], where ρ is the density and 2P = 1.8 × 10<sup>-5</sup> = 2ρ/2 × 10<sup>5</sup> where 2 × 10<sup>5</sup> is considered to be the molecular weight of the unvulcanized Viton A-HV polymer.

<sup>d</sup> Values of T<sub>g</sub> obtained from dilatometric determinations of temperature dependence of specific volume.

<sup>e</sup> Value from paper by E. E. Weir, W. H. Leser, and L. A. Wood, *J. Res. Natl. Bur. Std.*, **44**, 367 (1950).

servations: (1) a specimen did not dissolve in acetone during a 17-day period even though the volume fraction of rubber at swelling equilibrium was 0.015; and (2) creep occurred continuously at ambient temperature during a 5-month period under a stress of 70 psi; however, the specimen recovered to within a few per cent of its initial length when the load was removed and the specimen exposed to solvent vapors (followed by solvent removal) to promote recovery.

Ring-type specimens<sup>16</sup> were cut from sheets (~1.9 mm. thick) of the vulcanizates. Rings placed over supporting hooks were tested with an Instron tester at 7–10 crosshead speeds between 0.02 and 20 in./min. over extended temperature ranges. Each ring was placed in the temperature-conditioning cabinet 10 min. before a test was begun. During extension, the stress and strain around a ring are uniform, although the stress and strain at the inside circumference of a ring are greater than those at the outside circumference. To obtain the average stress, the retractive force was divided by the cross-sectional area of the ring. The strain at the point of average stress was computed from the crosshead displacement ΔL by the approximate equation ε = 2ΔL/C<sub>a</sub>, where ε is the strain, defined as the increase in specimen length divided by its initial length, and C<sub>a</sub> is the

average circumference of the unstretched ring. In the derivation of this equation, the change in the midpoint of a ring during a test is neglected; a more precise equation<sup>17</sup> is

$$\epsilon = (2\Delta L/C_a) - (\pi W_0/C_a)[1 - (1 + \epsilon)^{-1/2}] \quad (4)$$

where  $W_0$  is the initial width of the ring. For rings used in the present study, the neglect of the second term in eq. (4) gives data which are large by about 2.6% at small strains and by about 0.9% at a 300% strain. In obtaining  $\Delta L$  from a force-time (Instron) trace, a correction was made for the "toe," which occurs at the beginning of the trace. The correction, which is quite small, could be made accurately by extrapolating the convex down portion of the trace to zero force to establish the point of zero time.

Values of stress and strain were based on the dimensions of unstretched rings at 25°C. The neglect of the temperature dependence of the dimensions of specimens introduces an error in the data, especially at very high or very low temperatures. If the coefficient of cubical expansion of a specimen is  $6 \times 10^{-4}/^\circ\text{C}$ ., reported values of stress and strain at 230°C., for example, are large by factors of about 1.08 and 1.04, respectively.

## Results

The shape of a stress-strain curve, from a test made at a constant extension rate, reflects the inherent nonlinearity of the material and the continuous relaxation of stress during the test (unless the test is conducted under equilibrium conditions). The first step toward disentangling these effects consists of deriving stress-strain data at fixed values of time; such isochronal data show the strain-strain characteristics of the material at a specific state of relaxation. Isochronal data can be considered in terms of

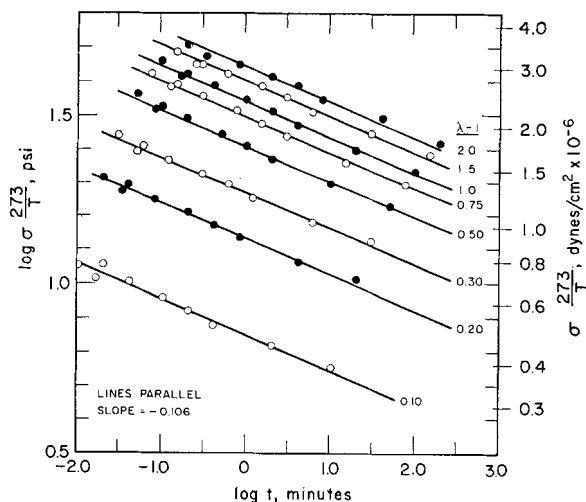


Fig. 1. Time dependence of stress-strain data from tests at different strain rates at 130°C. on Viton A-HV vulcanizate A-2.

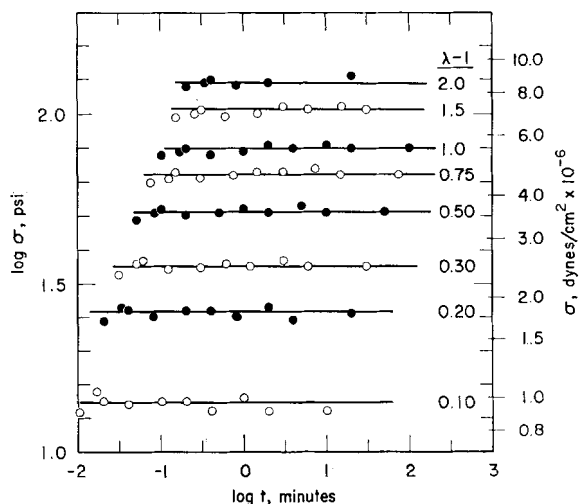


Fig. 2. Equilibrium stress-strain data from tests at different strain rates at 40°C. on butyl vulcanizate.

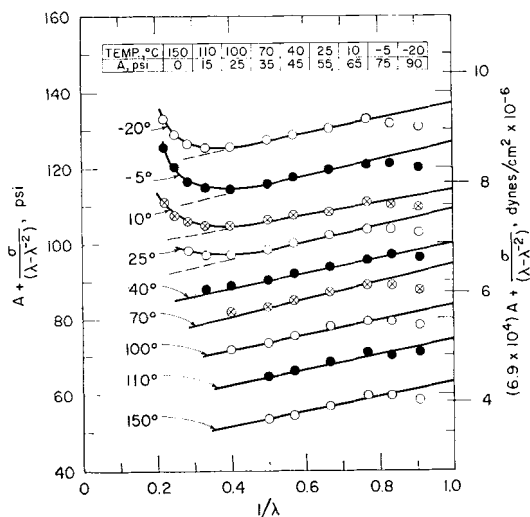
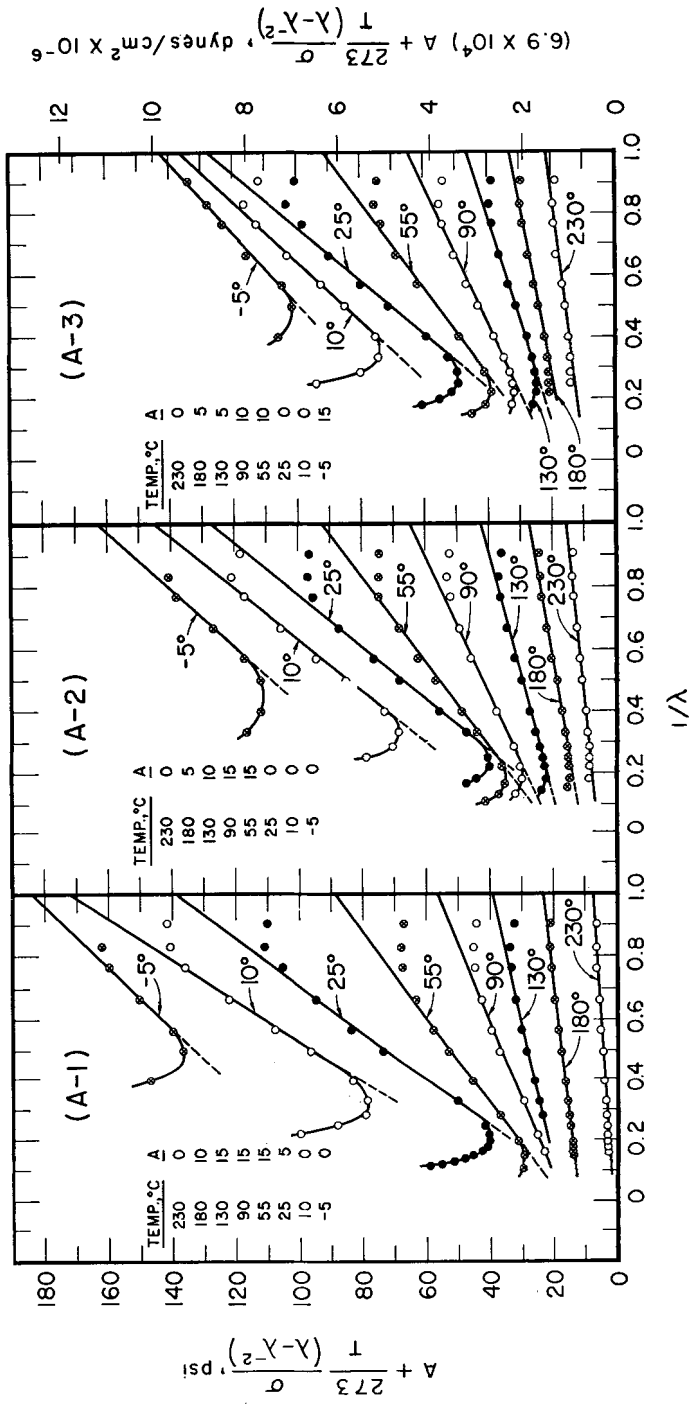
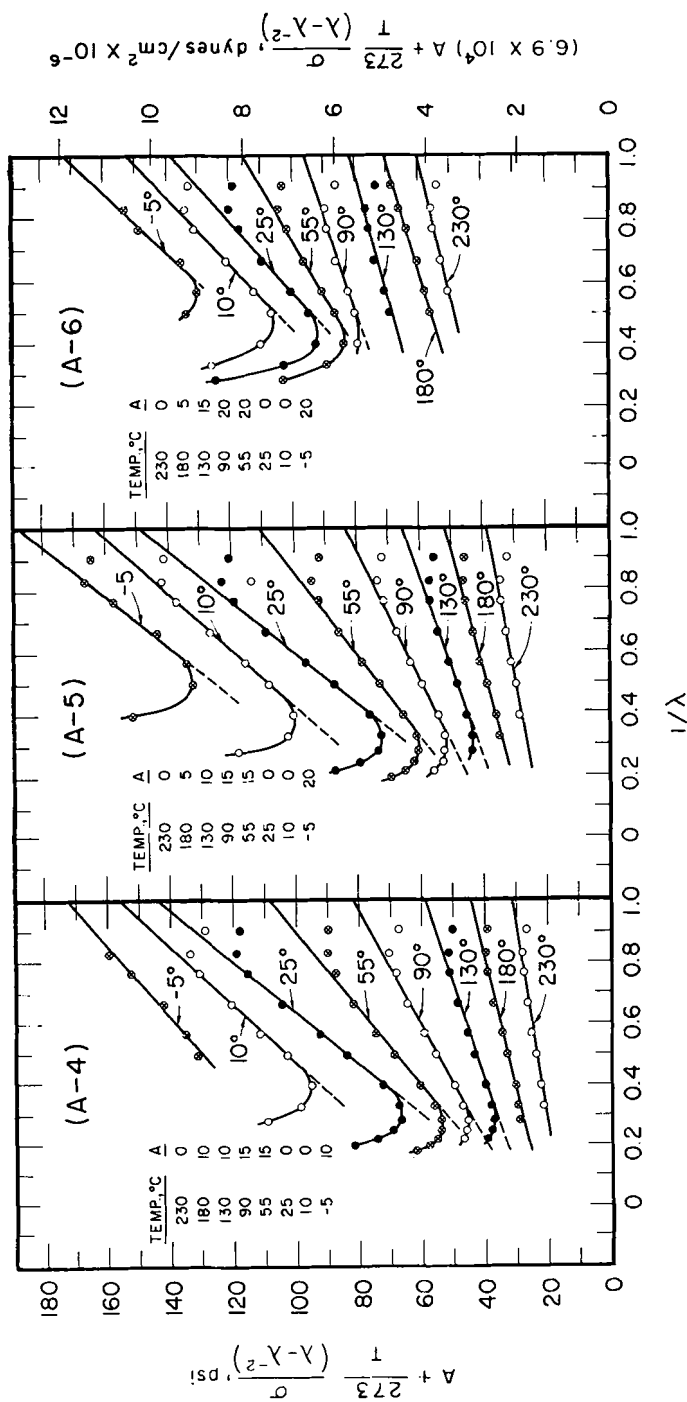


Fig. 3. Mooney-Rivlin plots of equilibrium data obtained on butyl vulcanizate at temperatures between  $-20$  and  $150^{\circ}\text{C}$ . ( $A$  is an arbitrary constant used to separate lines for clarity.)

constitutive equations [e.g., eq. (2) or (3)] which are based on equilibrium theory, although the significance of the parameters in the equation will differ from that of those from equilibrium data. In addition, the values of the parameters will depend not only on time—as well as on temperature—but also on the stress-strain history. That is, time-dependent parameters from data at a constant extension rate will not be the same as those from stress-relaxation or creep data, for example.







The method for deriving isochronal stress-strain data from curves determined at differing extension rates has been presented previously.<sup>18</sup> It consists of first obtaining the stress from each stress-strain curve at a set of preselected strains. Data at each value of strain are then displayed on plots of  $\log \sigma$  vs.  $\log t$ , where  $\sigma$  is the nominal stress (force divided by the cross-sectional area of the unstretched specimen) and  $t$  is the time;  $t = (\lambda - 1)/(d\lambda/dt)$  where  $\lambda$  is the extension ratio,  $\lambda - 1$  is the strain  $\epsilon$ , and  $d\lambda/dt$  the rate of extension. From such plots isochronal stress-strain data are obtained.

The time dependence of the stress at constant values of strain is illustrated by Figure 1, which shows data obtained on Viton A-HV vulcanizate A-2 at 130°C. and at crosshead speeds between 0.02 and 20 in./min. (The ordinate is  $\log \sigma 273/T$ , where  $T$  is the test temperature in °K.) The lines, which are drawn parallel, have a slope corresponding to a stress decay of about 24.4% per decade of time. Figure 2 shows data obtained on the butyl vulcanizate at 40°C. Essentially no points deviate from the lines of zero slope by more than 0.02 logarithmic unit (a 5% deviation). Although the lines indicate equilibrium behavior, a stress decay of 1%, or possibly even 3%, per decade of time could have occurred without being detected by the experimental procedure for obtaining data.

Plots like those in Figures 1 and 2 were prepared from data on the butyl, silicone, and Viton A-HV vulcanizates at temperatures in the respective ranges: -20 to 150°C.; -45 to 200°C.; and -5 to 230°C. For the butyl vulcanizate, the plots of  $\log \sigma$  vs.  $\log t$  showed<sup>16</sup> that some degradation occurred during tests at 120 and 150°C.; at times of 1 min. and less, the amount of degradation appeared to be relatively small. At -5 and -20°C. time-dependent behavior was observed, although at  $t \geq 1$  min. the data showed near-equilibrium behavior. Within the precision of the data, equilibrium behavior was found at all other test temperatures over the period covered by the tests, which was about three decades of time. For the silicone vulcanizate, equilibrium behavior was observed at all temperatures, except at -20, -35, and -45°C. some relaxation was evident at times less than 1 min. For the six Viton A-HV vulcanizates, equilibrium was not observed even at 230°C. and chemical degradation apparently did not occur during test periods. The relaxation rate decreased markedly with an increase in crosslink density; at 230°C. the rates of stress decay for A-1 and A-6 were, respectively, about 37 and 2.5% per decade of time.

From plots of  $\log \sigma$  vs.  $\log t$ , values of stress and strain at 1 min. were obtained and these were used to prepare plots of  $\sigma/(\lambda - \lambda^{-2})$  vs.  $1/\lambda$ , shown for the butyl vulcanizate in Figure 3 and for the six Viton A-HV vulcanizates in Figure 4. Temperature-reduced values of stress (i.e.,  $\sigma 273/T$ ) are used in Figure 4. Similar plots were prepared from data on the silicone vulcanizate.

Examination of Figures 3 and 4 shows that the data define reasonably good straight lines, especially at values of  $1/\lambda$  less than about 0.8. At

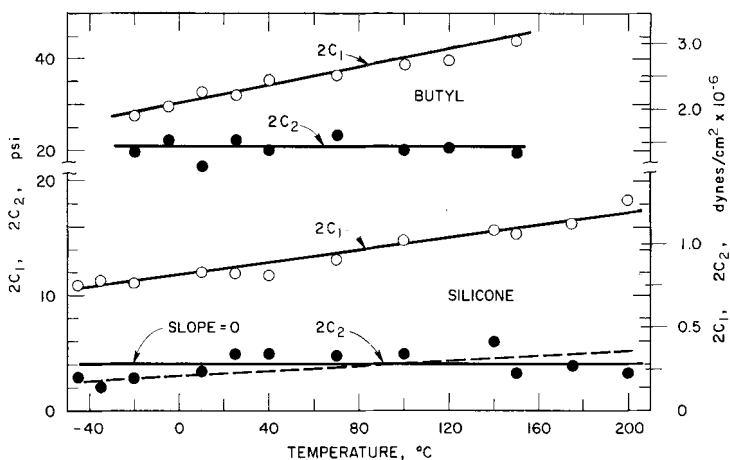


Fig. 5. Temperature dependence of  $2C_1$  and  $2C_2$  for butyl and silicone vulcanizates.

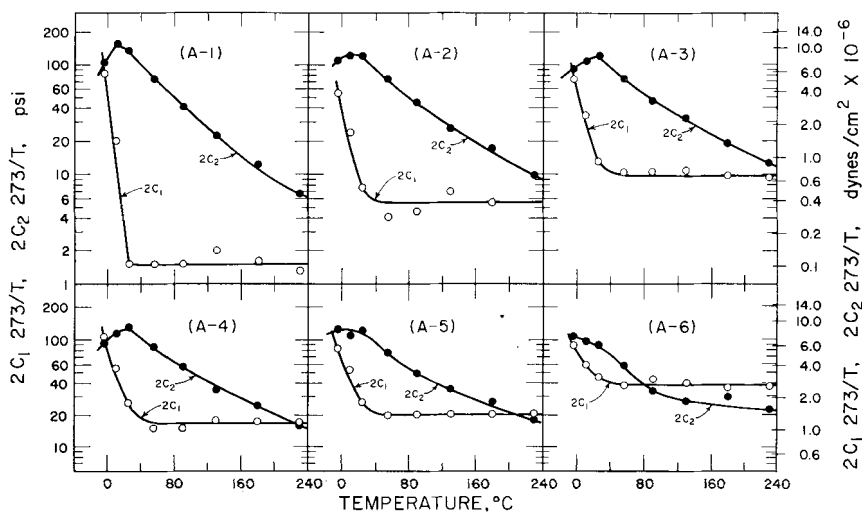


Fig. 6. Temperature dependence of 1-min. values of  $2C_1 273/T$  and  $2C_2 273/T$  for Viton A-HV vulcanizates.

values of  $1/\lambda$  greater than 0.8, the points tend to lie below the straight lines. However, the data, even at small values of  $\lambda$ , are quite typical of those reported in the literature; often data at values of  $1/\lambda$  greater than 0.8 are not reported. Because of the method used to obtain data for the present investigation, the results at small values of strain are not considered to be highly reliable. On the other hand, as discussed in the Introduction, it is expected that the slope of a Mooney-Rivlin plot will decrease significantly as  $\lambda$  approaches unity.

Values of  $2C_1$  and  $2C_2$  for the butyl vulcanizate, obtained from the slopes and intercepts of lines in Figure 3, are plotted against temperature in

Figure 5 along with similar data for the silicone vulcanizate. Temperature-reduced data for the Viton A-HV vulcanizates are in Figure 6. Other aspects of the stress-strain characteristics of the Viton A-HV (especially A-6), butyl, and silicone vulcanizates are considered elsewhere<sup>19</sup> along with their rupture characteristics.

### Discussion of Results

For the butyl and silicone vulcanizates, Figure 5 shows that  $C_1$  increases with temperature and that  $C_2$  is sensibly temperature independent. Although the values of  $C_2$  show some scatter, they definitely show no tendency to decrease with an increase in temperature. If  $C_2$  reflects only a deviation from equilibrium behavior, it should decrease somewhat over the extended temperature ranges covered by the experiments. Increasing the temperature from 0 to 200°C. is equivalent to increasing the experimental time scale by a factor of about  $10^5$ , if the activation energy ( $\Delta H_a$ ) for relaxation is 15 kcal. This value of  $\Delta H_a$  is a reasonable one for the butyl vulcanizate, since  $\Delta H_a$  for the viscous flow of a high molecular weight polyisobutylene decreases<sup>20</sup> from about 17 kcal. at 0°C. to 12 kcal. at 100°C. However,  $\Delta H_a$  for the viscous flow of a noncrosslinked poly(dimethyl siloxane) polymer has been found<sup>21</sup> to be 3.65 kcal. over the range -21 to 141°C. Also, in superposing values of the ultimate tensile properties determined on the silicone vulcanizate at various strain rates and temperatures, shift factors were obtained<sup>17</sup> which correspond to a constant  $\Delta H_a$  of 6.8 kcal. Because a  $\Delta H_a$  of 5 kcal. and a 200°C. temperature increase correspond to increasing the experimental time scale by a factor of only 15, it might be contended that a slow relaxation of the silicone vulcanizate would not have been detected.

In recent years attention has been directed toward determining  $[\partial \ln (f/T)/\partial T]$ , where  $f$  is the retractive force evaluated either at a constant specimen length  $L$  or at a fixed  $\lambda$ , and toward relating this derivative to  $d \ln \langle r^2 \rangle_0 / dT$  (see, for example, references 22-24). Although the present data on the silicone and butyl vulcanizates are not of sufficient precision to warrant an evaluation of  $d \ln \langle r^2 \rangle_0 / dT$ , the observed temperature dependence of  $C_1$  can be compared with reported results from force-temperature measurements. Such a comparison provides additional evidence that the  $C_1$  and  $C_2$  data for the silicone and butyl vulcanizates represent equilibrium behavior quite closely.

Values of  $\lambda$  used in deriving  $C_1$  and  $C_2$  from experimental data were obtained from the relation  $\lambda - 1 = (L - L_0)/L_0$ , where  $L_0$  is the unstretched length at 25°C. and  $L$  is the unstretched length at the test temperature. Thus  $[\partial \ln (f/T)/\partial T]$  obtained from the  $C_1$  and  $C_2$  data corresponds to conditions neither of constant length nor of constant  $\lambda$ ; for  $\lambda < 2$ , it corresponds somewhat more closely to conditions of constant  $\lambda$  than of constant length, but for  $\lambda > 2$ , the opposite situation exists.

To obtain an estimate of the temperature dependence of  $f$ , the following equation,<sup>10</sup> which is based on eq. (2), was used:

$$\left[ \frac{\partial \ln (f/T)}{\partial T} \right]_{\lambda} = \frac{1}{(C_1 + C_2/\lambda)} \left[ \frac{dC_1}{dT} + \frac{1}{\lambda} \frac{dC_2}{dT} \right] - \frac{1}{T} \quad (5)$$

This equation indicates that  $[\partial \ln (f/T)/\partial T]_{\lambda}$  is a function of  $\lambda$  which approaches  $[d \ln (C_1/T)/dT]$  as  $\lambda$  becomes infinitely large. The data of Roe and Krigbaum<sup>10,25</sup> on natural rubber and Viton A vulcanizates give\*  $[\partial \ln (f/T)/\partial T]_{\lambda}$ , which increases with an increase in  $\lambda$ , a result in agreement with eq. (5), provided  $d \ln C_1/dT > d \ln C_2/dT$ .

From the  $C_1$  and  $C_2$  data in Figure 5, the left side of eq. (5) was evaluated at the mean test temperature (80°C. for the silicone and 60°C. for the butyl vulcanizate) subject to the assumption that  $dC_2/dT = 0$ . For the silicone vulcanizate,  $[\partial \ln (f/T)/\partial T]$  was found to be  $-1.2 \times 10^{-3}$  at  $\lambda = 1.6$  and about  $-0.8 \times 10^{-3}$  at  $\lambda = \infty$ . Mark and Flory<sup>23a</sup> determined  $[\partial \ln (f/T)/\partial T]_L$  on four silicone vulcanizates and found that  $[\partial \ln (f/T)/\partial T]_L$  increases smoothly from about  $-1.5 \times 10^{-3}$  at  $\lambda = 1.34$  to  $-0.83 \times 10^{-3}$  at  $\lambda = 2.10$ . Their data give\*  $[\partial \ln (f/T)/\partial T]_{\lambda} = -0.5 \times 10^{-3}$ , and this temperature coefficient appears to increase slightly with increasing  $\lambda$ . Even though  $[\partial \ln (f/T)/\partial T]$  from the  $C_1$  and  $C_2$  data is associated with conditions intermediate between those of constant  $L$  and constant  $\lambda$ , it can be concluded that the values are comparable to the reported<sup>23a</sup> ones.

For the butyl vulcanizate, the  $C_1$  and  $C_2$  data give  $[\partial \ln (f/T)/\partial T] = -1.0 \times 10^{-3}$  at  $\lambda = 1.60$  and  $-0.28 \times 10^{-3}$  at  $\lambda = \infty$ . Reported values,<sup>23b</sup> determined at constant  $L$  at  $\lambda$  between 1.7 and 3.7, do not vary systematically with  $\lambda$ , and they range from  $-0.09$  to  $0.18 \times 10^{-3}$ ; the average value corresponds to  $[\partial \ln (f/T)/\partial T]_{\lambda} = 0.3 \times 10^{-3}$ . The disagreement between values reported and those from the  $C_1$  and  $C_2$  data is probably a result of the occurrence of a slight amount of degradation at the elevated test temperatures. Actually, if values of  $C_1$  at the higher temperatures are omitted, a line of increased slope can be drawn through the remaining points in Figure 5. This slope leads to values of  $[\partial \ln (f/T)/\partial T]$  which, although they depend rather strongly on  $\lambda$ , are in the same range as the reported ones. On the other hand, the present data for the butyl as well as the silicone vulcanizate can be brought into precise agreement with the published data by assuming that  $dC_2/dT$  is slightly positive.

Although the stress-strain data for the butyl and silicone vulcanizates are time independent within the precision of the experimental method, other studies<sup>26-28</sup> have shown that vulcanizates prepared by crosslinking high molecular weight polymers with conventional agents do not attain an equilibrium deformation under a constant load, regardless of the elapsed

\* The published<sup>10,23,25</sup> force-temperature data which are referred to in this paper were determined at constant  $L$  and at constant pressure  $P$ . Such data have been converted into force-temperature data at constant  $\lambda$  through use of the equation<sup>22</sup>  $[\partial \ln (f/T)/\partial T]_{P,\lambda} = [\partial \ln (f/T)/\partial T]_{P,L} + \beta(\lambda^3 + 2)/3(\lambda^3 - 1)$ , where  $\beta$  is the cubical thermal expansion coefficient. This equation is based on the assumption that eq. (1) is a valid equation of state. This assumption is probably not valid, as indicated by the data in this paper and by the data and discussion of Roe and Krigbaum.<sup>10</sup>

time or the temperature. Creep rates less than 1 to 2% per decade of time apparently have not been observed, and commonly the observed rate is considerably greater. In view of these observations, the present data on the butyl and silicone vulcanizates—as well as previously reported data on similar vulcanizates—undoubtedly do not, strictly speaking, represent equilibrium behavior. However, the present data have provided values of  $C_1$  and  $C_2$  over an unusually wide temperature range and the derived temperature dependence of  $C_1$  is in reasonable agreement with published force-temperature data over a more restricted temperature range. Since  $C_2$  for both vulcanizates shows no tendency to decrease with a temperature rise within the wide temperature range, it is unrealistic to attribute  $C_2$  solely to nonequilibrium effects.

In contrast to the behavior of the silicone and butyl vulcanizates, the Viton A-HV vulcanizates did not exhibit equilibrium behavior even at 230°C. One-minute values of  $2C_1273/T$  and  $2C_2273/T$  are shown in Figure 6 plotted on semilogarithmic coordinates. For each vulcanizate from slightly above 25 to 230°C.,  $2C_2273/T$  decreases markedly, the rate of decrease becoming less with an increase in crosslink density, whereas  $2C_1273/T$  is sensibly temperature independent. Below about 25°C.,  $2C_1273/T$  is strongly temperature and thus time dependent, undoubtedly because the terminal relaxation time of individual network chains becomes of the same magnitude as (and eventually, considerably longer than) the experimental time scale. This change in network characteristics is also reflected by the minima in the Mooney-Rivlin plots (Fig. 4) shifting toward smaller  $\lambda$  below 25°C. Above about 25°C. values of  $2C_1273/T$  for each vulcanizate (neglecting several values for A-1 and A-2) fit quite precisely the lines of zero slope in Figure 6. These lines correspond to the values of  $2C_1273/T$ , which are given in Table I and which, as mentioned previously, increase in direct proportion to the amount of curing agents in each vulcanizate.

The observation that the pronounced relaxation shown by the six Viton A-HV vulcanizates above 25°C. is reflected primarily, if not entirely, by a change in  $C_2$  is in general accord with the limited results of Gent and Rivlin<sup>29</sup> and of Rivlin and Saunders,<sup>30</sup> who studied various vulcanizates at ambient temperature in shear, torsion, and uniaxial tension. In those instances in which the mechanical response was time dependent, they found that relaxation affects only  $\partial W/\partial I_2$  and that  $\partial W/\partial I_1$  remains unchanged. They concluded that  $\partial W/\partial I_1$  can be identified with that given by the statistical theory of rubberlike elasticity. However,  $C_1$  and  $C_2$  cannot be equated to  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$ , respectively. Even if  $\partial W/\partial I_1$  is a constant under equilibrium conditions, it has been pointed out<sup>4</sup> that both  $C_1$  and  $C_2$  will depend on  $\partial W/\partial I_2$ , which in turn is a function of  $\lambda$ . Thus, in considering time- and temperature-dependent data, it might be expected that  $C_1$  as well as  $C_2$  will depend on time, although it might also be expected that  $C_1$  will be only slightly time dependent. Because the time dependence of the data on the Viton A-HV vulcanizates was not evaluated,

it is not known whether relaxation indeed causes a small change in  $C_1$ . The present results do show, however, that the time dependence of  $C_1$ —if in fact  $C_1$  is time dependent—must be exceedingly slight, otherwise  $C_1$  would not increase in direct proportion to the absolute temperature.

To consider  $C_1$  further, it will be assumed that  $C_1$  is time independent and that its temperature dependence is given by  $dC_1/dT \cong C_1/T$ . Subject to these assumptions, it follows from eq. (5) that  $[\partial \ln (f/T)/\partial T]_\lambda$  should approach zero as  $\lambda$  becomes infinitely large. Roe and Krigbaum<sup>25</sup> have reported force-temperature data on a Viton A vulcanizate which at 45°C. had nearly the same  $2C_1/273/T$  as that for A-6. (Viton A gum stock has a lower primary molecular weight than Viton A-HV.) Their data show that at 45°C.  $[\partial \ln (f/T)/dT]_\lambda$  increases from about  $0.9 \times 10^{-3}$  at  $\lambda = 1.22$  to  $1.3 \times 10^{-3}$  at  $\lambda = 1.62$ ; this increase implies that  $[d \ln (C_1/T)/dT]$  from equilibrium data is greater than zero. However, a critical comparison of their data with those from the present work is not warranted, because they studied a different Viton vulcanizate by a different method and especially because the amount by which  $[d \ln (C_1/T)/dT]$  may deviate from zero cannot be accurately judged because of the limited accuracy of the present data. Also, there is the possibility, as mentioned above, that  $C_1$  may be slightly time dependent. On the other hand, Roe and Krigbaum report that  $2C_1 = 3.32$  kg./cm.<sup>2</sup> and  $C_2/C_1 = 0.87$  at 45°C. For comparison, the curves in Figure 6 from 1-min. data on A-6 show that  $2C_1 = 3.12$  kg./cm.<sup>2</sup> at 45°C. and that  $C_2/C_1$  decreases from about 0.87 at 90°C. to 0.60 at 230°C. Admittedly, some degradation or additional cure may have occurred at 230°C., although this seems rather unlikely, because the specimens were exposed to the 230°C. environment for only 11 min. and because  $2C_1/273/T$  for all six vulcanizates was sensibly constant over a range of about 200°C. In view of the persistent relaxation indicated by Figure 6, it is possible that the data of Roe and Krigbaum represent the material in a continuously varying state of relaxation; if this is true, their results at  $\lambda = 1.62$  should most nearly represent equilibrium behavior. Although the present data show that  $C_2$  continues to decrease even at 230°C., it is not suggested that  $C_2$  vanishes at equilibrium.

Even above 25°C. the dependence of  $C_2$  on  $C_1$  is quite complex. Since the molecular origin of  $C_2$  is unknown, only the qualitative trends will be pointed out. An inspection of tabulated data shows: (1) at 180 and 230°C.,  $C_2$  increases with an increase in  $C_1$ ; (2) at 130, 90, and 55°C.,  $C_2$  passes through a maximum as  $C_1$  increases; and (3) at 25 and 10°C.,  $C_2$  tends to decrease with an increase in  $C_1$ . (No clear trend is shown at -5°C.) On the other hand, at all temperatures except possibly -5°C.,  $C_2/C_1$  decreases with an increase in  $C_1$ ; above about 25°C., it also decreases with a temperature rise. Both the increase in  $C_2$  (at 180 and 230°C.) and the decrease in  $C_2/C_1$  with an increase in  $C_1$  are qualitatively similar to those found by Kraus and Moczygemba<sup>15</sup> for sulfur vulcanizates of polybutadiene of a given primary molecular weight. Their 10-hr. data, obtained only at 25°C. on vulcanizates prepared from polybutadiene polymers with dif-

ferent primary molecular weights, gave values of  $C_2/C_1$ , which vary from 3.0 to 1.1; for the Viton A-HV vulcanizates,  $C_2/C_1$  varies from 90 to 0.6.

Although the molecular significance of  $C_2$  is unknown, the time and temperature dependence of  $C_2$  for the Viton A-HV vulcanizates above about 25°C. may reflect a slow rearrangement of network junction points and associated chains in the manner proposed and treated in a semiquantitative manner by Bueche.<sup>31</sup> According to his treatment, the extent and the time scale of the process increase with an increase in the fraction of dangling chains; qualitatively, these trends are shown by  $C_2$ , especially at 180 and 230°C. The slow relaxation process may also result from the rearrangement of entanglements, as considered by Kraus and Moczygamba<sup>15</sup> and also by Ferry<sup>14</sup> and his associates, who have studied the phenomenon under small, sinusoidally varying, deformations. It would appear that the molecular mechanism associated with relaxation at elevated temperatures is related to the existence of  $C_2$  under equilibrium conditions. Various proposals to explain the existence of  $C_2$  are considered in the recent review article by Krigbaum and Roe.<sup>32</sup>

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### Résumé

On a déterminé les courbes tension-élongation, à différentes vitesses d'élongation et à différentes températures, de caoutchouc au butyle et de caoutchouc silicone non-chargés et aussi de si caoutchoucs hydrofluorés (Viton A-HV) contenant de  $0.90$  à  $12,2 \times 10^{-6}$  mole de ponts efficaces par unité de volume de gel de caoutchouc. A partir de courbes isochrones effectuées à un temps d'une minute, on a déterminé les paramètres  $C_1$  et  $C_2$  de l'équation de Mooney-Rivlin. On a obtenu les résultats suivants: les caoutchoucs au butyle et les caoutchoucs au silicone sont caractérisés entre  $-20^\circ\text{C}$  et  $+150^\circ\text{C}$ , et  $-45$  et  $+200^\circ\text{C}$  respectivement par une valeur du paramètre  $C_1$  qui augmente avec la température avec une vitesse qui est en bon accord avec les données de la littérature (courbes de force-température). Comme le paramètre  $C_2$  ne dépend pratiquement pas de la température dans les températures déterminées, on conclut que le paramètre  $C_2$  représente le valeur limite que l'on obtiendrait à l'équilibre. On a étudié la dépendance du temps pour les caoutchoucs Viton-A-HV entre  $-5^\circ\text{C}$  et  $230^\circ\text{C}$ . Pour chaque caoutchouc d'expression  $C_1 273/T$  est indépendant de la température entre  $25^\circ\text{C}$  et  $230^\circ\text{C}$  et croît lorsque la température diminue en-dessous de  $25^\circ\text{C}$ . Si on en excepte les plus basses températures, l'expression  $C_2 273/T$  décroît lorsque la température augmente. On constate cependant que la vitesse de diminution devient moindre progressivement lorsque la densité de pontage augmente. Au-dessus de  $25^\circ\text{C}$ , le rapport  $C_2/C_1$  qui varie de  $90$  à  $0.6$ , diminue lorsque la température et la densité de pontage augmente. La dépendance de la température du rapport  $C_2 273/T$  semble résulter surtout de mouvements moléculaires caractérisés par des temps de relaxation beaucoup plus longs que les temps de relaxation maximum des chaînes prises individuellement.

### Zusammenfassung

Zugspannungs-Dehnungsdaten wurden bei verschiedenen Dehnungsgeschwindigkeiten und Temperaturen an ungefüllten Butyl- und Silikonvulkanisaten sowie an sechs Fluorkohlenwasserstoff-(Viton A-HV)-vulkanisaten mit einem Gehalt an effektiven Netzwerkketten zwischen  $0,90$  und  $12,2 \times 10^{-6}$  Mol pro Volumeneinheit Gelkautschuk bestimmt. Aus den ein-Minuten isochronen Daten wurden die  $C_1$  und  $C_2$ -Werte in der Mooney-Rivlin Gleichung abgeleitet. Bei den Butyl- und Silikonvulkanisaten nimmt

$C_1$  mit der Temperatur von  $-20$  bis  $150^\circ\text{C}$  bzw.  $-45$  bis  $200^\circ\text{C}$  mit einer Geschwindigkeit zu, die mit Literaturdaten von Kraft-Temperaturmessungen annehmbar übereinstimmt. Da  $C_2$  in diesen ausgedehnten Temperaturbereichen sich als temperaturunabhängig erweist, scheint  $C_2$  unter Gleichgewichtsbedingungen eine endliche Grösse zu besitzen. Ein zeitabhängiges Verhalten zeigten die Viton A-HV-Vulkanisate zwischen  $-5$  und  $230^\circ\text{C}$ . Bei jedem Vulkanisat ist  $C_1 273/T$  zwischen etwa  $25$  und  $230^\circ\text{C}$  temperaturunabhängig, nimmt aber unterhalb etwa  $25^\circ\text{C}$  mit fallender Temperatur zu. Ausgenommen bei den tiefsten Temperaturen, nimmt  $C_2/273/T$  mit steigender Temperatur ab und die Abnahmegeschwindigkeit verringert sich stetig mit zunehmender Vernetzungsdichte. Überhalb  $25^\circ\text{C}$  fällt das Verhältnis  $C_2/C_1$ , das etwa zwischen  $90$  und  $0,6$  liegt, mit Temperatur- und Vernetzungsdichtezunahme ab. Das zeitabhängige Verhalten von  $C_2 273/T$  scheint primär durch molekulare Prozesse bedingt zu sein, deren Relaxationszeit beträchtlich länger ist als die Endrelaxationszeit der individuellen Ketten.