
TEMPERATURE DEPENDENCE OF ELASTIC CONSTANTS OF RUBBERS

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SYNOPSIS

On the specially designed dynamometer with automatic control of $\lambda = \text{constant}$ condition at temperature alteration (λ is the extension ratio), there were studied the temperature dependence of stress, f , in uniaxial tension tests of butyl and butadiene-acrylonitrile vulcanisates at various λ . Temperature coefficients of C_2 constant in the Mooney-Rivlin equation, calculated from these data, are represented reasonably well by the semiempirical formula

$$\frac{d \ln(C_2/T)}{dT} = \frac{-\beta}{1 - \beta(T - T_0) - 0.25}$$

(β is the bulk thermal expansion coefficient, T is the absolute temperature, T_0 is the constant temperature), derived using molecular theory which revealed the origin of the C_2 term and the empirical generalization of the dependence of C_2 on swelling degree.

The published data on the temperature dependence of C_2 and the methods of further experimental examination of conception suggested are discussed.

INTRODUCTION

According to the classical rubber-like elasticity theory¹ the dependence of equilibrium stress, f , at uniaxial tension on the extension ratio λ should obey the equation

$$f = \nu kT \frac{\langle h^2 \rangle}{\langle h^2 \rangle_0} (\lambda - \lambda^{-2}) \quad (1)$$

where ν is the number of effective network chains in a unit volume, k is the Boltzmann constant, T is the absolute temperature, $\langle h^2 \rangle$ and $\langle h^2 \rangle_0$ are, respectively, the mean-square end-to-end distance of network chains at $\lambda = 1$ and temperature T and the same quantity for the chains when free of network constraints at the same temperature. If the chains contain energetically non-equivalent rotational isomers, their content changes with temperature which leads to a change of $\langle h^2 \rangle_0$ and to the appearance of the energetic stress component, f_e . Thus, studying the dependence of stress on temperature one can

obtain f_e and the difference of energies of rotational isomers, ΔU . This concept, at first proposed by Volkenshtein and Ptitsyn,² has been the origin of an extensive series of studies into the thermoelasticity of elastomers.^{3,4} Further interest in these studies has been stimulated by theoretical calculations of thermoelastic properties that were carried out for polymers of different chemical structure.⁵

Since, f denotes the retractive force assigned to the cross-sectional area of underformed sample at some fixed temperature, then

$$\frac{f_e}{f} = -T \left[\frac{\partial \ln (f/T)}{\partial T} \right] + \frac{\beta \cdot T}{3} = T \frac{\partial \ln \langle h^2 \rangle_0}{\partial T} \quad (2)$$

where β is the bulk thermal expansion coefficient.

The last derivative of eq. (2) is connected directly with the type and energy difference of the rotational isomers constituting the chain and, hence, it need not depend on λ .

Contrary to this theoretical prediction, f_e/f changes markedly with strain.⁶ One may see the reasons for this phenomenon in the fact that formula (1) does not agree with experiment. It is known that uniaxial tension data fit quite well the Mooney-Rivlin equation:^{7,8}

$$f = 2C_1(\lambda - \lambda^{-2}) + 2C_2(1 - \lambda^{-3}) \quad (3)$$

the first term of which coincides with eq. (1). This provides the basis⁹ on which to identify $2C_1$ with the elastic constant of the statistical rubber-like elasticity theory:

$$2C_1 = \nu kT \frac{\langle h^2 \rangle}{\langle h^2 \rangle_0} \quad (4)$$

If one adopts this suggestion, then formula (2) transforms to

$$\frac{f_e}{f} = -T \left[\frac{\partial \ln (C_1/T)}{\partial T} \right]_{\lambda, \nu} + \frac{\beta T}{3} = T \frac{\partial \ln \langle h^2 \rangle_0}{\partial T} \quad (5)$$

giving f_e/f independent on deformation. In the limited studies¹⁰⁻¹³ devoted to separate investigation of the temperature dependences of C_1 and C_2 , it has been found that they depend on temperature in different ways. A satisfactory explanation of this fact has not been given yet due to the unknown nature of the additional term in eq. (3).

In the present paper, we intend to discuss the dependencies pointed out on the basis of the theory presented in the preceding article.¹⁴

THEORY

The classical rubber-like elasticity theory holds that the joining of chains into network puts constraints upon the arrangement of their ends only. Therefore, the theory accounts for only the entropy change connected with the

alteration of chain end-to-end distances at network deformation that leads to eq. (1). Such an approach is equivalent to the use of a model of "shadow chains" which are not only volumeless but also able to pass freely through each other like shadows on a wall.

In a real network such a situation does not exist. At sufficiently rapid deformation, all the linear chain dimensions, including its transversal dimensions, change affinely.¹⁵ Insofar as the transversal chain dimensions do not depend on its end-to-end distances in the framework of Gaussian approximation, then together with the redistribution of chain sections lengths the establishing of network equilibrium will be accompanied by the recovery of transversal chain dimensions. This process cannot continue to the end because the chains drawn together upon deformation will hinder its completion due to the impossibility of their passing through each other. Insofar as each chain is surrounded by a sufficiently great number of neighbors then such steric obstructions will frequently occur along its contour. Mean-square distance between the chain segments and the straight line connecting its ends, $\langle r^2 \rangle$, by which we will characterize the transversal chain dimensions, will differ by the same quantity in the undeformed state, $\langle r^2 \rangle_0$, even when the strained network is at equilibrium. This leads to the extra entropy change which depends on the extension ratios in a different way than the entropy change connected with the increase of end-to-end distances as this latter distance and $\langle r^2 \rangle$ change dissimilarly during deformation.

The theory based on these premises¹⁴ describes well the regularities of various types of deformation and allows one to explain qualitatively a rather wide range of experimental data. In particular, for the nominal stress at uniaxial tension it gives the dependence,

$$f = 2C_1(\lambda - 1/\lambda^2) + K \left[-\frac{1}{\lambda^2} + \frac{3}{2} \frac{\lambda}{\lambda^3 - 1} + \frac{\lambda^4 - 4\lambda}{2(\lambda^3 - 1)^{3/2}} \tan^{-1}(\lambda^3 - 1)^{1/2} \right] \quad (6)$$

which is very close to the Mooney-Rivlin eq. (3) at $0.2 < \lambda^{-1} < 0.9$, i.e., within the whole interval of deformations practically accessible for measurements. Here C_1 has its usual meaning given by formula (4) and K is unknown since in direct theoretical calculation to assign any value it is necessary to know the spatial arrangement of the steric obstructions.

At this point one may say only that it is proportional to the absolute temperature T , the number of chains in a unit volume, ν , and does not depend on unperturbed transversal dimensions, $\langle r^2 \rangle_0$ (see eq. (18) in ref. 14). Remember that the presence of $\langle h^2 \rangle_0$ in the expression for C_1 is connected with the fact that $\langle h^2 \rangle$ and $\langle h^2 \rangle_0$ are different in the initial undeformed state. As for the transversal dimensions, its values for unstrained chains in the network coincide with the corresponding ones for isolated chains, and the front-factor for K is equal to unit.

Consequently, the deviation of K from the direct proportionality to absolute temperature may be connected only with the alteration of the spatial arrangement of steric obstructions. If a sample is in an equilibrium state then

such alteration may be connected only with the change of sample geometry. In particular, it may be an isotropic deformation taking place with the swelling and thermal expansion of the sample. Being unable to theoretically calculate the variation of K upon the isotropic deformation we may attempt to establish a connection between the above two types of deformation and thereby to verify the premises of the theory briefly outlined above.

For a series of rubbers it has been found by Gumbrell et al.¹⁷ that the variation of C_2 with swelling may be described by the empirical formula

$$C_{2 \text{ swell.}} = C_{2 \text{ dry}} \times 1.33(V_r - 0.25) \quad (7)$$

where V_r is a volume fraction of rubber in a swelling vulcanizate. There are no data in the literature as to whether this dependence is valid for any rubber or whether it changes with temperature variation. On the assumption that formula (7) is a precise one for a certain temperature T_0 and the variation of K at isotropic deformation does not depend on the reasons responsible for the deformation, one may write, taking into account the above-mentioned factors influenced by K ,

$$K(T) = \nu kTg \{V_r[1 - \beta(T - T_0)] - 0.25\} \quad (8)$$

where g is a factor dependent on spatial arrangement of steric obstructions.

The dependence of $\psi = (f/2) \times (\lambda - \lambda^{-2})^{-1}$ on λ^{-1} calculated by eq. (6) is a nonlinear one at $\lambda^{-1} < 0.2$. Therefore, the procedure of finding the constants for this equation is slightly different from the treatment of experimental data according to the Mooney-Rivlin equation. If A and B denote the segments cutting off on ordinates at $\lambda^{-1} = 0$ and $\lambda^{-1} = 1$, respectively, by the continuation of the linear part of $\psi(1/\lambda)$ plot, then¹⁴

$$C_2 = B - A; \quad C_1 = A + 0.1(B - A) = A + 0.1C_2; \quad K = 3.21C_2 \quad (9)$$

The values of C_1 and C_2 cited below have been calculated by these formulas.

From eqs. (8) and (9) it follows that for dry vulcanizates,

$$\frac{C_2(T)}{C_2(T_0)} = \frac{K(T)}{K(T_0)} = \frac{T[1 - (T - T_0) - 0.25]}{0.75T_0} \quad (10)$$

i.e., C_2 is always increasing more slowly than the absolute temperature.

EXPERIMENTAL

Sample

The strip form specimens were cut from press cured sample sheets (about 0.1 cm thick). The recipes and conditions are listed in the Table I. The values of the bulk thermal expansion coefficients are also listed there. Two pair of thin ink strokes, about 2.5–3.0 cm apart, were marked on each sample.

TABLE I
Recipes and Curing Conditions of the Vulcanizates studied

Recipe (by weight)	P	Q
Butyl rubber	100	—
Butadiene-acrylonitrile rubber (butadiene/acrylonitrile 60:40)	—	100
Stearic acid	3.0	1.5
Captax	0.6	0.8
Thiuram	1.3	—
Zinc oxide	5.0	5.0
Sulfur	2.0	1.0
Temperature(°C)	143	143
Time (min)	40	50
Bulk thermal expansion coefficient, $\times 10^4$ (deg ⁻¹)	5.52	4.92

Apparatus

The measurements were carried out on the specially designed dynamometer which automatically supported the condition $\lambda = \text{const}$ approximately during the test time. The dynamometer construction is sketched in Figure 1. The upper platform 1 with a strain gauge 2, to which the upper clamp was attached by its supporting rod 3, was connected by means of Duralumin rods 6 and 7 to the lower platform 4, in which the lower clamp supporting rod 5 was squeezed. The length of Duralumin rods was chosen in such a manner that an increase of the distance between the clamps due to thermal expansion of the rods corresponded precisely to the increase of specimen length in the undeformed state. Such a choice of rod length provided automatic support of

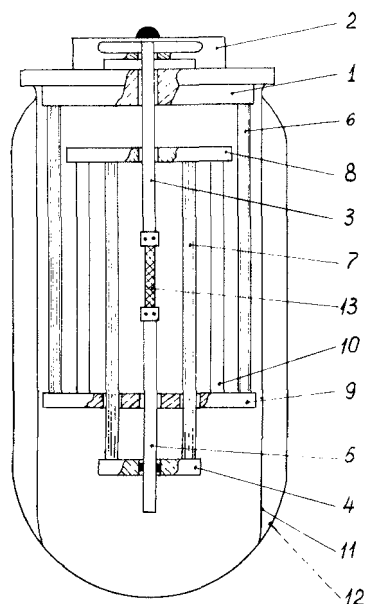


FIG. 1. Scheme of the dynamometer for full explanations, see the text.

the condition $\lambda = \text{const}$ at λ close to 1. This condition was partially violated as λ increased, however, it was not of primary significance as the necessity of precise support of $\lambda = \text{const}$ condition lessened with the increase of λ .

The direct calculations showed that the relative error of $\psi = f/2(\lambda - \lambda^{-2})$ was approximately equal to $0.02 \Delta T\%$, i.e., its maximum value did not exceed 0.8% at the maximum deviations from room temperature which were measured in the present work. No corrections for deviations from the condition $\lambda = \text{const}$ were introduced which suggests that these values were within the limits of experimental errors.

Owing to the great difference between the thermal expansion coefficients of Duralumin and rubbers, the rods must be long enough to provide dimensions of specimens convenient for operation. To avoid having the device too large, Duralumin rods were manufactured as a composite. For that reason two extra circular platforms 8 and 9 were introduced which had been rigidly attached to each other by the fused quartz rods 10. The rods 3 and 5 were manufactured from the same material. The temperature coefficient of the device, i.e., the increment of the distance between the clamps upon the increase of temperature by a degree, were equal to $1.37 \times 10^{-4} \text{ cm deg}^{-1}$ with two pairs of rods, 6 and 7 (as sketched in Fig. 1), and to $0.71 \times 10^{-4} \text{ cm deg}^{-1}$ when platforms 8 and 9, rods 7 and 10 were removed and the lower platform 4 was attached directly to rods 6.

The whole dynamometer, except the strain gauge, was placed into glass vessel 11 surrounded by a thermostating glass jacket 12. Alcohol of a desired temperature was circulated through the annular space between the vessel and the jacket by means of an ultrathermostat. The temperature in the vessel was measured by a thermocouple. The output from the strain gauge transducer, amplified and recorded by a high-grade millivoltmeter, varied linearly with applied force.

Test Procedure

The distance between the sample marks in the initial and strained states was measured by means of a cathetometer to an accuracy of 0.01 mm. The actual accuracy of measurements was somewhat lower. The result was considered satisfactory if the difference between two parallel measurements did not exceed 0.03 mm. All the tests were carried out on the dynamometer with rods 6 only, i.e., with temperature coefficient equal to $0.71 \times 10^{-4} \text{ cm deg}^{-1}$. Proceeding from the values of β cited in Table I, the distances between the clamps were chosen equal to 38.6 and 43.4 mm, respectively, for samples P and Q. Two parallel lines, the stated distances apart, were marked on each sample and then a given test specimen was clamped along the line locations.

After this, the lower clamp was fixed at the position corresponding to the desired minimum strain and the specimen was allowed to relax for 16–18 hr at room temperature. The temperature was then brought to 60°C and after standing under these conditions for an hour, the first measurement was made. The subsequent measurements at 40, 20, 0, and -20°C were also made

following an hour of thermostating of the specimens. In some cases the measurements were made at intermediate temperatures. In order to more rapidly obtain the desired temperature two ultrathermostats were used. The special experiments were carried out in order to control the reproducibility of the data from cooling and heating cycles. A reasonably good coincidence was obtained and all further measurements were carried out only at subsequent temperature decreases.

After completion of one such temperature cycle, the strain was increased up to the next value and in 16–18 hr the new series of measurements was completed. The tests were usually carried out at deformations equal to 10, 25, 40, 65, and 100%. The measurements at the contraction of samples were not made. All the tests were repeated on parallel specimens. In all the cases a close agreement was obtained for the character of temperature dependencies, but the numerical values of the stress diverged, in some cases, to as much as 7% apparently at the expense of the errors in measuring of the cross-sectional areas of the samples.

RESULTS AND DISCUSSION

The temperature dependencies of the stress for butadiene-acrylonitrile rubber (sample Q), at the different values of pointed out near the curves, are shown in Figure 2. Plots of $\psi = (f/2)(\lambda - \lambda^{-2})^{-1}$ against $1/\lambda$, derived from

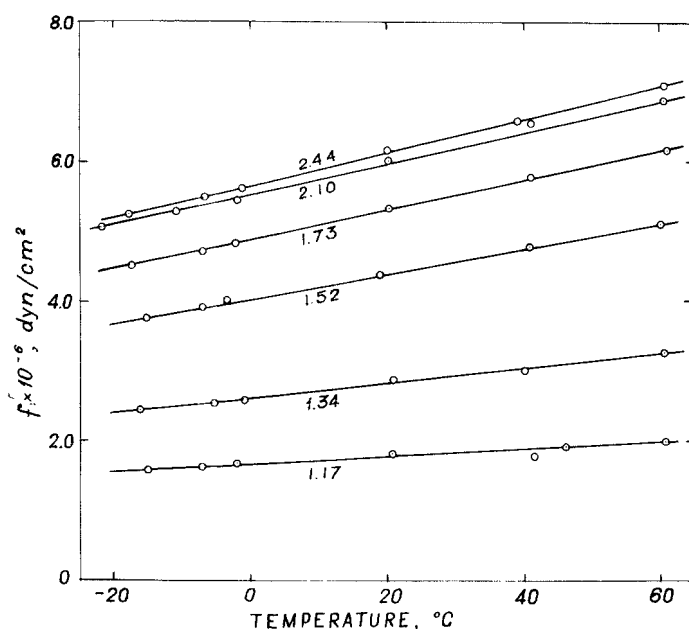


FIG. 2. Temperature dependencies of nominal stress f in uniaxial extension for butadiene-acrylonitrile rubber vulcanizate (sample Q). Numbers near the curves indicate extension ratios.

these data for temperatures of 60, 40, 25, 10, -5 , and -20°C , are shown in Figure 3. The values of C_1 and C_2 calculated from these plots by eq. (9) are plotted in Figure 4 as a function of the absolute temperature. The dotted lines passing through absolute zero are also shown there. One can see from the plots that C_1 increases more rapidly and C_2 more slowly than the absolute temperature does.

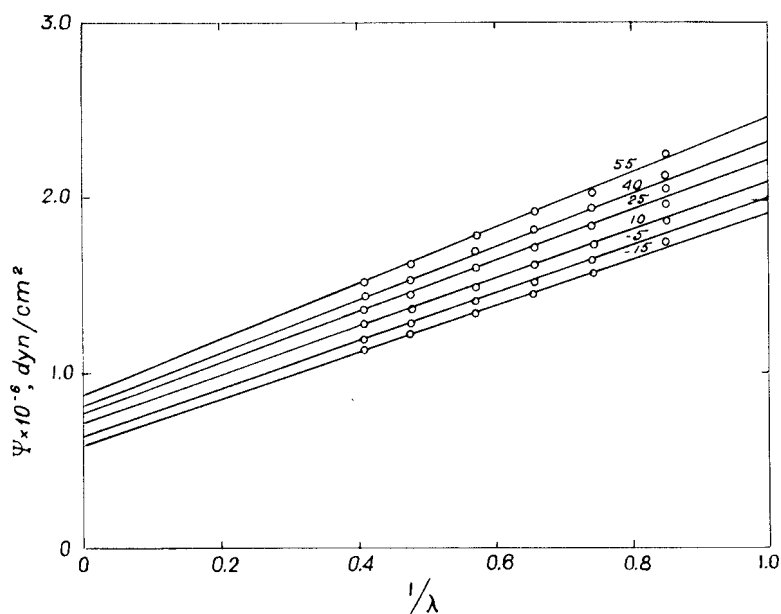


FIG. 3. Mooney-Rivlin type plots for sample Q at various temperatures (pointed out near the curves).

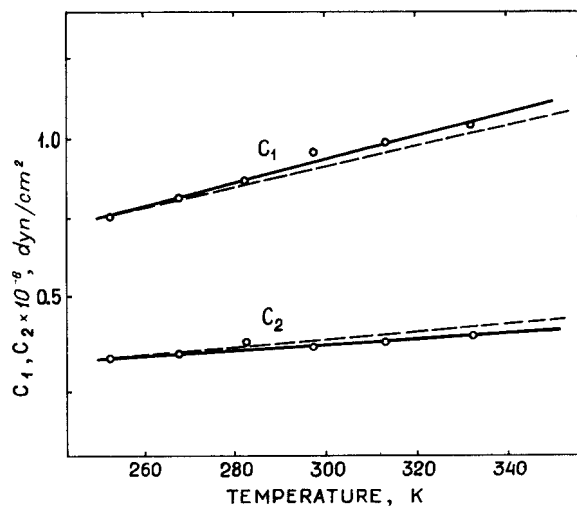


FIG. 4. Temperature dependencies of C_1 and C_2 for butyl rubber vulcanizate (sample P). The dotted lines correspond to direct proportionality to T .

In the same way the temperature dependencies of C_1 and C_2 for butyl rubber were obtained. Plots for it are shown in Figure 5. Figure 6 shows the results obtained for natural rubber by Shen and co-workers,¹⁸ which were recalculated using eq. (9). From these graphs, one can see that C_2 always increases more slowly than the absolute temperature does without respect to whether C_1/T decreases (natural rubber) or increases (the samples P and Q) as temperature increases.

The temperature dependencies of C_2 analyzed in terms of eq. (10) practically coincide with the experimental ones for samples P and Q. As for Shen's data, the theoretical curve (shown in Fig. 6) falls markedly lower for experimental data.

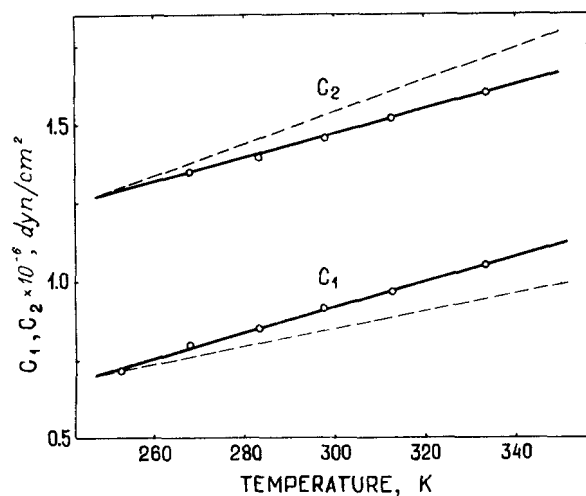


FIG. 5. Temperature dependencies of C_1 and C_2 for butadiene-acrylonitrile rubber vulcanizate (sample Q). The dotted lines correspond to direct proportionality to T .

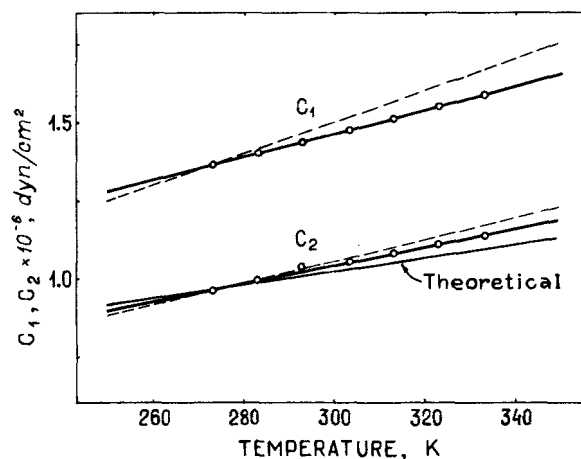


FIG. 6. Temperature dependencies of C_1 and C_2 for natural rubber calculated from data of Shen and co-workers.¹⁸ The dotted lines correspond to direct proportionality to T . The theoretical dependence is calculated from eq. (8).

The values of $d \ln (C_1/T)/dT$ and $d \ln (C_2/T)/dT$, derived from the data of Figures 4-6, and the value of $[d \ln (C_2/T)/dT]_{\text{theor}}$ were calculated by

$$\left[\frac{d \ln (C_2/T)}{dT} \right]_{\text{theor.}} = \frac{-\beta}{1 - \beta(T - T_0) - 0.25} \quad (11)$$

obtained by differentiation of eq. (8), are listed in Table II. The same table shows the data of Roe and Krigbaum¹⁰ and Yamamoto and co-workers¹¹ for natural rubber, and Yamamoto and co-workers¹¹ for two butadiene rubbers, PBI and PB II. The temperature coefficient of C_2/T for these polymers as calculated in terms of β values cited in ref.¹¹ In Table II, the values of $d \ln (C_2/T)/dT$ are slightly different from those of the original works because C_1 were recalculated in terms of eq. (9).

TABLE II.
Temperature Coefficients of C_1/T and C_2/T

Polymer	$\frac{d \ln (C_1/T)}{dT} \times 10^3$	$\frac{d \ln (C_2/T)}{dT} \times 10^3$	$\left[\frac{d \ln (C_2/T)}{dT} \right]_{\text{theor}} \times 10^3$	ν_0
Butyl rubber (sample P)	3.8	-0.81	-0.77	0.96
Butadiene-acrylonitrile rubber (sample Q)	11.9	-0.76	-0.68	0.92
Natural rubber				
(Shen and co-workers ¹⁸)	11.0	-0.46	-0.92	1.70
(Roe and Krigbaum ¹⁰)	-0.2	-3.30	-0.92	0.32
(Kamamoto and co-workers ¹¹)	-0.3	-9.20	-0.92	0.29
Butadiene rubbers				
(Yamamoto and co-workers ¹¹)				
PB I	0.45	-1.95	-0.89	0.39
PB II	0.62	-2.53	-0.89	0.36

For all the data taken from other works^{10,11} one observes sharp discrepancies between the values of $d \ln (C_2/T)/dT$ derived from experimental data and those calculated in terms of eq. (11). This may be the result of several reasons. First of all, the large variations between the data of different authors for natural rubber are striking. If according to Shen and co-workers the temperature coefficient of C_2/T is half as large as the theoretical one, from the data of Roe and Krigbaum it is three times as much, and Yamamoto and co-workers have even observed a decrease of C_2 with increasing T . It would be tempting to explain these discrepancies by experimental errors especially as contradictory results have been obtained for other polymers too. Thus, according to Smith,¹² $C_2/T = \text{const}$ for butyl rubber contrary to the data obtained in present work. Indeed, even for very careful measurements of f and λ , the accuracy of C_1 and C_2 obtained proves to be disappointingly low.

However, a closer examination of various data for natural rubber permits one to see a certain pattern in these discrepancies. Thus, the samples studied by Shen and co-workers have $C_2 = 1 \times 10^6 \text{ dyn cm}^{-2}$, those of Roe and Krigbaum have $C_2 = 0.86 \times 10^6 \text{ dyn cm}^{-2}$, and those of Yamamoto and co-

workers have $C_2 = 0.42 \times 10^6 \text{ dyn cm}^{-2}$, i.e., the absolute value of $d \ln (C_2/T)/dT$ increases with decreasing C_2 . Confirmation of such regularity can be found in the literature¹⁹ where poly(cetylmethacrylate) possessed the least value of C_2 from the series of poly(alkylmethacrylates) studied and there C_2 decreases with temperature.

Such regularity may be interpreted using the theoretical concepts presented in the beginning and the empirical formula (7). In the preceding paper,¹⁴ it was pointed out that increasing chain breakdown or the growth of chain side-groups diminish the number of steric obstructions which leads to a decrease of C_2 , as happens with swelling. For such networks it is natural to introduce into eq. (8) an additional factor $V_0 \leq 1$ describing this decrease.

$$K(T) = 3.21 C_2 = \nu k T_g \{V_0 V_r [1 - \beta(T - T_0)] - 0.25\} \quad (12)$$

One can see that this leads simultaneously to an increase of absolute value of $d \ln (C_2/T)/dT$. The values of V_0 showing the coincidence of this formula with experiment are listed in the last column of Table II. The presence of $V_0 > 1$ for Shen's data must not be considered as a refutation of the expressed theories. This discrepancy may be connected both with experimental errors and with imperfection of the initial formula (7).

As to V_0 , for the majority of other polymers, its values seem to be too small but we have no criterion for its objective estimation. The conclusive experiments should be the studies of: (i) the temperature dependence of C_2 in swollen rubbers and (ii) the dependence of C_2 on V_r for the rubbers with essential discrepancies between experimental and theoretical values of $d \ln (C_2/T)/dT$.

Thus, the main qualitative prediction of the theory that C_2 has to increase more slowly than the absolute temperature is met for all the polymers studied. As for the quantitative comparison of the theory with experiment, further experimental investigations need to be carried out along the above-mentioned lines.

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