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Transient Changes in Topology and Energy on Extension of Polybutadiene Networks

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Transient Changes in Topology and Energy on Extension of Polybutadiene Networks

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Summary

The theory of elasticity of polymer networks has been developed along two lines. The phenomenological approach leads to the Mooney-Rivlin relation between stress and extension ratio for uniaxial extension. The statistical theory of elasticity, based on a model for polymer molecules, predicts a similar relation with one of the constants zero. Actual elastic properties of rubbers do not agree fully with either theory.

Experimental results are reported obtained with quantitatively cured polybutadiene and polyisoprene vulcanizates. These data are near-equilibrium results through the use of a cyclic stress sequence which largely eliminates the influence of long-time creep. The dependence of the initial modulus and the parameters of the Mooney-Rivlin relation on the chemical nature and the degree of branching of the polymer, the type of cross-links, and temperature has been investigated. A possible relation between the energy component of the elastic force and one of the parameters is discussed.

These results as well as those in the literature refer to irreversible processes. It is proposed that this irreversibility results from friction accompanying slippage of chain entanglements. This mechanism is compatible with the observed dependences. It is concluded that the variation of elastic properties with elongation is due to changes in network topography.

Some observations are made on the topological changes of vulcanizate networks at very high elongations. Similarities are pointed out between reinforcement by stress crystallization and by addition of carbon black. The effect of blacks is attributed mainly to preferential adsorption on the carbon particles of short network chains which become overstressed at high deformation. On adsorption the kinetic energy of these particular chains will be dissipated in the form of heat of adsorption.

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Examples are given of the applicability of F. Bueche's relation between extension of the sample and that of the elastomer matrix in a filled vulcanizate. This equation differs from that based on Einstein's relation for the viscosity of suspensions, which has been shown to be applicable in other filled rubbers. The difference between the two relations may be associated with the absence or presence of chemical bonding of elastomer to filler.

Network topography has an influence on the ultimate properties of vulcanizates. Polybutadiene samples in which the cross-links are single bonds break at lower elongation than those with equal concentrations of cross-links consisting of 18-atom chains.

INTRODUCTION

Because the experiment is such a simple one, the routine determination of the elasticity of a rubber is the measurement of the modulus of elongation. Very frequently this modulus is determined at both 100 and 300% extension. That *two* values are used to roughly characterize the rigidity of an elastomer is indicative of the fact that tension elongation curves of various rubbers have different shapes. This may not be surprising at first glance, but it is indeed unexpected from the molecular theory of rubber elasticity.

The theory of elasticity has been developed along two lines. Physicists have treated this property phenomenologically; i.e., they have derived relations which describe elastic behavior by treating rubber as an isotropic elastic continuum. The equilibrium of all forces acting on an infinitesimal volume of material is considered. From conditions of symmetry and from boundary conditions general equations have been derived which relate the forces acting on an elastic body with the resulting deformations. For small, but finite, deformations these relations are most simply expressed in terms of the elastically stored energy W, and the strain invariants I_n, which are simple functions of the principal extension ratios. If stress and strain are linearly related, one can develop W in a power series of I_n, and on differentiation of this series one obtains the following relation for incompressible materials in uniaxial extension:

$$\tau/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2\lambda^{-1} + 6C_3(\lambda - 1)(1 - \lambda^{-2}) + \cdots \quad (1)$$

where τ is the stress per undeformed cross section, λ the extension ratio, and C_n constants. It is usual to consider only the first two terms of this series expansion. The resulting relation is known as the Mooney-Rivlin equation (*1,2*). Here the ratio $\tau/(\lambda - \lambda^{-2})$ will loosely be called shear modulus for convenience, although the two quantities are only equal under special conditions.

Another approach to the theory of elasticity is a mechanistic one based on a model representing polymer molecules. Physical chemists have tried to relate the macroscopic deformation of rubber with the deformation of individual polymer molecules and have attempted to derive the relation between body forces and the stresses deforming molecules. The detailed molecular structure of a vulcanizate is a very complex one. Long chains of polymer molecules, randomly interconnected by cross-links, form a network which is in a state of violent thermal turmoil. In the molecular theory of elasticity such a network is represented by a dynamic model consisting of chains of rods, representing segments of polymer molecules, freely jointed to one another and, in addition, occasionally and randomly connected by cross-links to neighboring chains of rods.

It can be calculated from the configurational rearrangement on extension of the chains of rods that, in the absence of energetic interactions between the molecules, stress and extension ratio are related by (*3,4*)

$$\tau = (\overline{r_n^2}/\overline{r_0^2})[\nu]RT\{(n^{1/2}/3)\mathscr{L}^{-1}(\lambda/n^{1/2}) - (n^{1/2}/3)\lambda^{-3/2}\mathscr{L}^{-1}[1/(\lambda n)^{1/2}]\} \quad (2)$$

where $\overline{r_n^2}$ is the mean-square end-to-end distance of chains between cross-links; $\overline{r_0^2}$ the mean-square end-to-end distance of free, undeformed chains; $[\nu]$ the concentration of chains between cross-links; n the average number of statistical links (rods) in the chains between cross-links; R the gas constant; T the absolute temperature; and $\mathscr{L}^{-1}$ the inverse Langevin function.

As long as the end-to-end distances between neighboring cross-links are appreciably smaller than the contour lengths of the chains connecting these cross-links, the expression in the braces is about equal to $\lambda - \lambda^{-2}$. At high elongations a fraction of the chains approaches full extension and hence the force required to further elongate such chains increases very rapidly. This increase is expressed by the term in the braces, which increases rapidly for large extension ratios. If the difference between $\overline{r_n^2}$ and $\overline{r_0^2}$ is ignored for the time being, Eq. (2) reduces to

$$\tau/(\lambda - \lambda^2) = [\nu]RT \tag{3}$$

for small and medium elongations.

In the following comparison of these theories with experimental data we shall consider only isotropic materials unless otherwise stated. It will be assumed that the rubbers used here are incompressible. In ordinary gum vulcanizates elongated to 100%, the fraction of the total force due to the increase in volume is of the order of 10^{-4}. Therefore, neglecting the compressibility of the rubbers is quite justified.

In Fig. 1 examples are given of the shapes of Mooney-Rivlin curves predicted by the continuum and the molecular-statistical theories. In the top part of the figure the continuum theory is represented in first approximation by the first two terms, and in second approximation by three terms of the right side of Eq. (1) with $C_1 = C_2 = 10C_3$. In Fig. 2 examples are shown of experimental curves for natural rubber and for *cis*-1,4-polybutadiene vulcanizates. Neither theory is seen to agree fully with the observed curves. The two

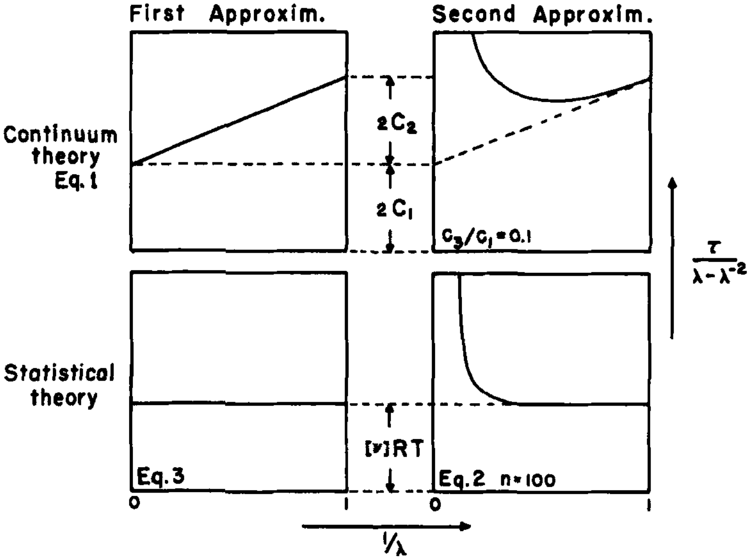

FIG. 1. Mooney-Rivlin curves corresponding to Eq. (1) (with $C_1 = C_2$ and left side $C_3 = 0$, right side $C_3 = 0.1C_1$), Eq. (3), and Eq. (2) (with $n = 100$).

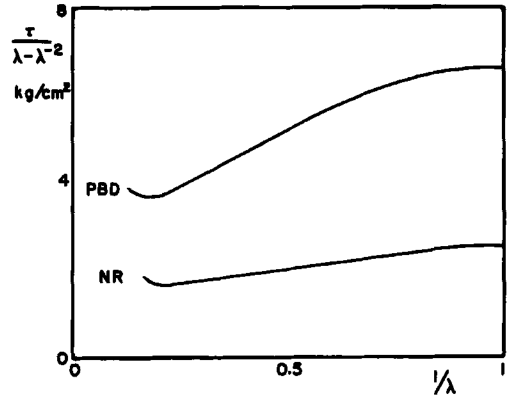

FIG. 2. Examples of experimental Mooney-Rivlin curves for polybutadiene (PBD) and natural rubber (NR). Chain concentrations are 0.071 and 0.069 mole/liter, respectively.

polymers of Fig. 2 are chemically very similar and are cured to the same extent with the same cross-linking agent. Nevertheless, the stress elongation relations are seen to be markedly different. It seems that the detailed chemical nature of the polymer or the fine topographical structure of the network is of importance in determining elastic response.

The work reported here was undertaken in the hope that it would contribute to an undetstanding of the phenomena which give rise to the observed deviations from elasticity theories.

EXPERIMENTAL

Polymers

Polybutadienes A and B with *cis*-1,4 contents of 92.8 and 96.5% have intrinsic viscosities in toluene at 30°C of 3.57 and 2.29, respectively. From their molecular-weight distributions, obtained by elution from a Baker-Williams column, the number-average molecular weights were determined. They are 3.0×10^5 and 2.3×10^5, respectively. Polybutadiene A, which was synthesized with the aid of a titanium salt containing Ziegler catalyst, is a linear polymer, and sample B, prepared with a catalyst containing cobaltous salt and a mixture of aluminum dialkyl monohalide and aluminum monoalkyl dihalide, has a few long-chain branches per molecule (5).

The natural rubber sample was obtained by milling Pale Crepe for 15 min at 30°C. The polymer, which is completely soluble, has an intrinsic viscosity of 2.84. The number-average molecular weight calculated from this viscosity and the relation given by Mullins and Watson (6) is 2.2×10^5.

Vulcanization

The vulcanizates were prepared by means of reaction with decamethylene dismethylazodicarboxylate (DMDADC). This reagent introduces cross-links by addition of both ends of the carboxylate molecule to α-carbon atoms of polydiolefins. It has been used earlier by Flory et al. (7), who presented evidence for its stoichiometric reaction. Polymer and DMDADC are mixed in solution. Because of the high reactivity of the curing agent, it is necessary to evaporate the solvent at low temperatures to avoid cross-linking of polymer molecules in solution, where their configuration is different from that in bulk. The vulcanization reaction with polyisoprene is notably faster than with polybutadiene. The samples were prepared by mixing solutions of polymer and of reagent in ether at −20°C, pouring the solution on mercury and evaporating the solvent at that temperature. The resulting films, which were soluble, were vulcanized by slowly heating to 60°C.

Other samples were prepared by reaction with cumene hydroperoxide (DCP) in a press at 145°C for 2 hr. To suppress cross-polymerization 10 parts of antioxidant was added to the reaction mixture (8). The reagent used was 4,4′-methylene bis(2,6-di-tert-butyl phenol), Antioxidant 702, Ethyl Corp. This additive was removed after cure by extraction with a 70:30 mixture of ethanol and toluene. Prior to heating the compound mixture was allowed to relax in the press for 72 hr at room temperature. Inspection with the polarizing microscope shows that the sheets, prepared following these methods, are free of internal stresses and may be considered isotropic.

The chain concentration of the vulcanizate network ($[\nu]^*$) was calculated from the concentration of the cross-linking agent $[X]$, using the following relation (9):

$$[\nu]^* = 2g\{[X] - g\rho \times 10^3/\bar{M}_n\} \qquad \text{mole/liter}$$

where g is the gel fraction, ρ the density of the vulcanizate, and $\bar{M}_n$ the molecular weight of the raw polymer.

Procedures

Samples in the shape of the common commercial rubberbands were died out from the vulcanized sheets. The circumference and width of the bands is 127 and 1.7 mm, respectively. The thickness of the bands was determined from the other dimensions, the weight of the sample (0.1 to 0.2 g) and the density of the vulcanizates: 0.911 for polybutadiene and 0.914 for natural rubber. The bands were suspended by means of Teflon rings with U-shaped cross section in the center tube of a condenser through which water of constant temperature was circulated. Weights were hung from similar rings inserted at the lower end of the sample band. A very small amount of silicone oil was used to reduce friction between sample and ring. Smith (*10*) has found that with these precautions the sections of the band encircling the rings elongate to the same extent as the free, vertical parts of the band.

Shortly after deformation creep can be very considerable. After longer waiting periods the rate of creep is low, but usually impractically long times are required for extensions to approach steady values. In our measurements we have followed a loading procedure

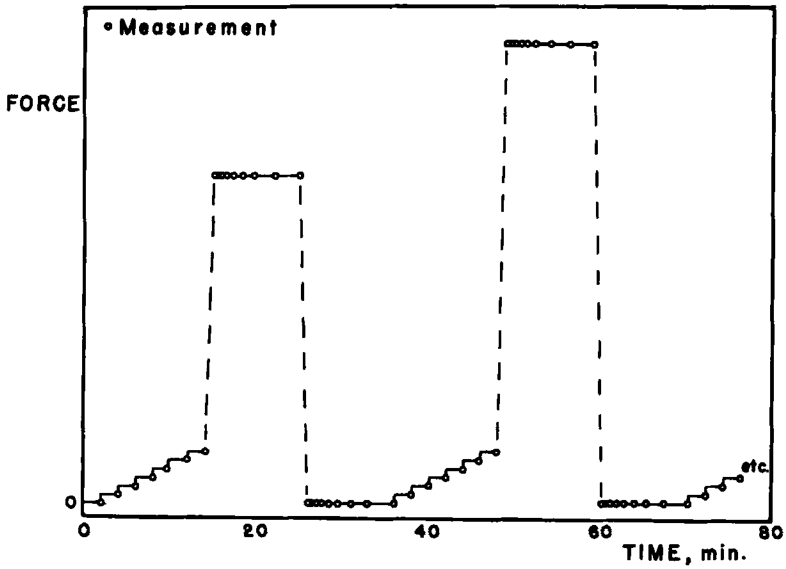

FIG. 3. Diagram of the stress cycles to which the samples are submitted.

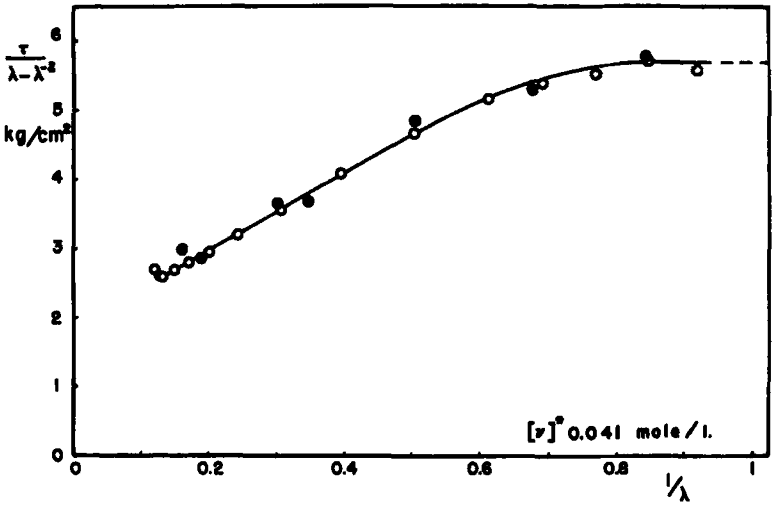

FIG. 4. Mooney-Rivlin plot for polybutadiene A, chain concentration 0.041 mole/liter. ○, Results from deformation of a single sample following the stress-cycle pattern shown in Fig. 3; ●, results from deformation of seven new samples which had not been deformed before.

which allows fast creep to take place and which eliminates to a large extent the influence of that part of the creep governed by long retardation times. Figure 3 shows this loading pattern; the circles indicate length measurements. The rest length of the specimen is determined before each elongation. The sample is allowed to creep under tension for 10 min and is allowed to recover after removal of the force for the same time period. The rest length of the specimen is then determined again. The effective rest length during extension is taken to be the average of the rest lengths before and after deformation.

This procedure gives reproducible results. The data in Fig. 4 show that it effectively eliminates the influence of the mechanical history of the specimen. The open circles are data resulting from deformation of a single specimen following the loading pattern described, and each of the filled circles represent data obtained with new samples which had never been deformed. The creep behavior of the samples between ⅓ and 10 min after applying the load is well represented by straight lines on a plot of elongation vs. the logarithm of the time elapsed since application of the force (t). It follows from this linear relation that the ratio t/τ_1 is constant, where

τ_1 is the retardation time of an equivalent Voigt element. The values of t/τ_1 are shown in Fig. 5 (note expanded scale of ordinate). Those of the individual samples, which have no history of deformation, are seen to fall close to the curve drawn through the values obtained from a single sample, deformed according to the loading procedure used here. The shape of this curve is related to that of the relaxation-time spectra at various stages of elongation. Whatever the significance of this shape, it may be concluded that the influence of long time creep and creep recovery on the behavior of the samples is very small. This is confirmed by a few measurements in which the time allowed for creep was 100 times longer than normal. These results are the same within experimental error as those obtained following the regular procedure. On the other hand, in experiments conducted at a constant rate of extension of 2 min^{-1}, which is some 100 times faster than for our loading pattern, the stresses were up to 15% higher, depending on the elongation.

In the stress-temperature measurements the sample was stretched between the pan of an automatic balance and a laboratory jack. Before beginning the measurements the sample was kept stretched for 16 hours at the desired elongation. Equilibrium data were obtained at each temperature by varying the elongation ϵ between about 0.98ϵ and 1.02ϵ and measuring the stress at six points between these limits. No hysteresis was detectable within this small range. These sets of measurements were repeated at seven different temperatures between −20 and +40°C. The results were not affected by the sequence of variations in temperature or by an additional waiting period of 16 hr.

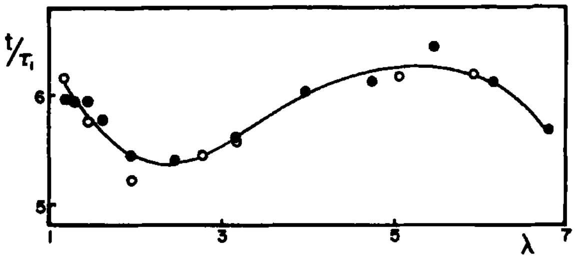

FIG. 5. Comparison of the creep behavior between ½ and 10 min expressed by the ratio t/τ_1 as a function of extension ratio λ, for a sample following the stress-cycle pattern (●) and for individual new samples which had not been deformed before (O).

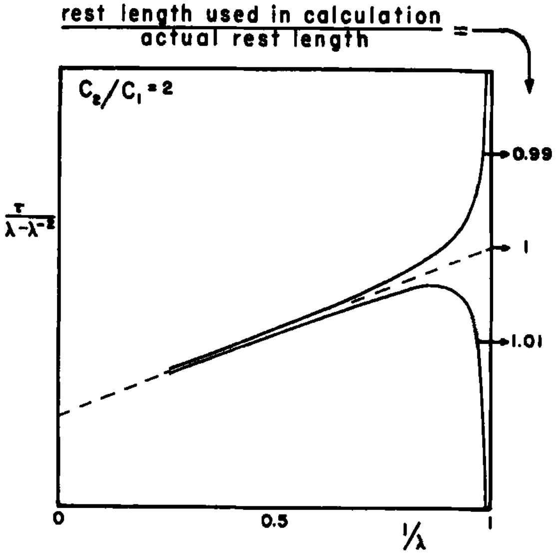

FIG. 6. Mooney-Rivlin plots calculated with an error in the rest length of 1% ($C_2 = 2C_1$).

It is worth mentioning that even the weakest cross-linked samples recovered after high elongations to within a few tenths of 1% of their original lengths. It was also established that the swelling ratios of the samples before and after the mechanical measurements are the same. Therefore, the networks are not damaged by high deformations.

It may be concluded that the present data represent near-equilibrium results on isotropic samples.

RESULTS AND DISCUSSION

For discussion of the experimental results it is expedient to distinguish between regions of low, medium, and high extensions.

Low Extensions

It is often not realized that the Mooney-Rivlin plot of the shear modulus $\tau/(\lambda - \lambda^{-2})$ vs. the reciprocal extension ratio requires a high accuracy of the experimental data at low extensions. Figure 6 shows this sensitivity. The curved lines have been calculated according to the continuum theory [Eq. (1) with $C_2 = 2C_1$ and

$C_3 = 0$] with an error of 1% in the rest length of the specimen. Obviously only very accurate data are of value in the region of small deformations. In this investigation of the elasticity of polybutadiene the elongations resulting from six different small forces were measured repeatedly (8 to 14 times). The largest of these elongations was between 2 and 7%. From the averages of these extensions the rest lengths of the specimen were determined assuming one of the following stress-strain relations:

(A) $\tau \propto (\lambda - 1)$
(B) $\tau_a \propto (\lambda - 1)$
(C) $\tau \propto (\lambda - \lambda^{-2})$ cf. Eq. (3)
(D) $\tau \propto (2C_1 + 2C_2\lambda^{-1})(\lambda - \lambda^{-2})$ cf. Eq. (1)

where τ is the force/cross section of the undeformed specimen, τ_a the force/cross section of the elongated specimen, and λ the extension ratio.

From these rest lengths, which differ one from another, sets of elongation values were calculated. Plots of the tensile forces versus the four functions of the extension ratio of relations A to D were fitted with least-square lines and the standard deviations from these lines were calculated. (In fitting the data to relation D, values of C_2 obtained over a wide range of elongations were used.) The Mooney-Rivlin plots of the above stress-strain relations, shown in

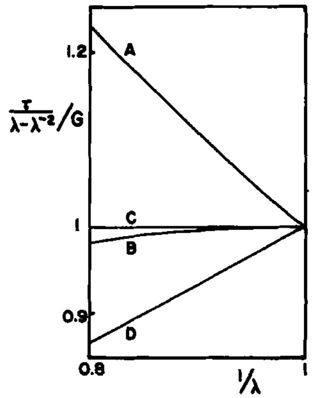

FIG. 7. Normalized Mooney-Rivlin plots at small extensions for four different stress-strain relations. G is the initial shear modulus. A, $\tau \propto (\lambda - 1)$; B, $\tau_a \propto (\lambda - 1)$; C, $\tau \propto (\lambda - \lambda^{-2})$; D, $\tau \propto (2C_1 + 2C_2\lambda^{-1})(\lambda - \lambda^{-2})$.

Fig. 7, are seen to differ markedly. The average standard deviations, in per cent elongation, of 20 series of 60 measurements each are 0.034, 0.025, 0.024, and 0.091% for the relations A, B, C, and D, respectively. It follows from these values that the data are best fitted by relations B or C. In spite of the high degree of accuracy attained, we cannot distinguish between Hookean (B) and neo-Hookean (C) elastic behavior. From the assumptions which enter into the continuum theory one would expect this theory to hold best at small extensions, yet relation D, the simplest two-parameter expression of the continuum theory, does seem to apply at small deformations.

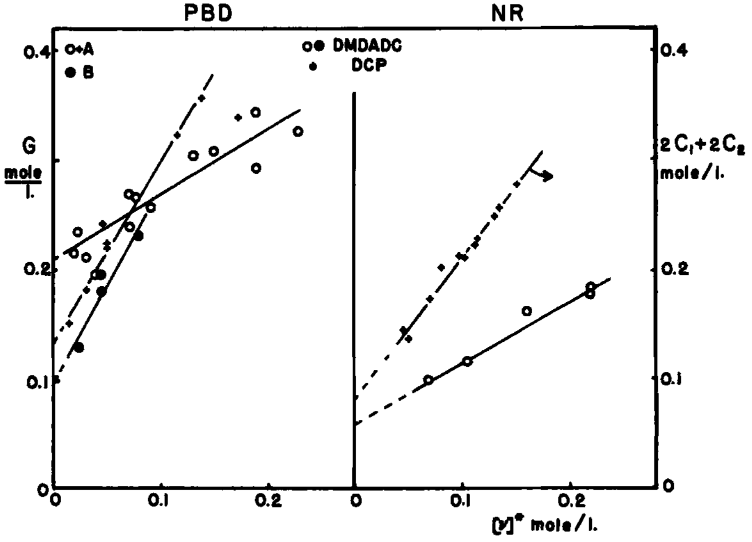

FIG. 8. Values of initial shear modulus G at 25°C as a function of chain concentration $[\nu]^*$ for polybutadienes A and B and for natural rubber. For peroxide-cured natural rubber [data of Bristow (*11*)] the sum $2C_1 + 2C_2$ is shown instead of G.

In Fig. 8 the values of the initial shear modulus G are shown as a function of the chain concentration $[\nu]^*$, calculated from the chemistry of the vulcanization reaction and corrected for loose chain ends and sol fraction. The results for peroxide-cured natural rubber are those of Bristow (*11*). Since no accurate data are available for the initial shear modulus of these materials, the sum $2C_1 + 2C_2$ has been plotted instead of G. There is little difference between this sum and G for the azocarboxylate-cured natural rubber samples. For easy comparison with chain concentration, modulus values have been expressed in units of RT ($T = 298°K$) and thus have dimensions of a concentration.

It is obvious that there are more chains elastically effective than one would expect from the chemical network density. This excess of active chains has been attributed to chain entanglements trapped by the vulcanization reaction. Since G is so much larger than $[\nu]^*$ there must be either a very large number of weakly effective entanglements, or the entanglements must be so tight that even at small deformations the sliding of chains past each other at the entanglement "points" is so restricted that these contact points act as cross-links.

FIG. 9. Schematic diagram of a selected portion of a vulcanized network.

Figure 9 is a schematic diagram of a selected portion of a vulcanizate network flattened to two dimensions. It is possible to trace many paths, following chains from cross-link to cross-link, starting and ending in the same cross-link A. The lengths of these closed paths varies greatly. Case and Wargin (*12*) have calculated that the shortest of all these loops passes only through a few tens of cross-links. The closed line ABPA in the diagram follows one of the relatively short loops of all the possible paths through A. The heavy lines show the interlooping of this closed path with other closed loops. These other loops may of course penetrate through the A loop at any point of the "surface" encompassed by the A loop. Only a few interloopings close to the border of the A loop surface are shown in the figure. This is done not only for the sake of clarity but it seems probable that at small deformations only these border interloopings result in tight entanglements of chains acting as additional cross-links. Thus each *pair* of heavy-drawn chains contributes *four* chains to the network.

The diagram is also presented to illustrate that addition of chemical cross-links does not, in general, produce more entanglements or interloopings. Linking the chain of the A loop at P with the dashed strand of chains Q merely restricts the interloopings to a smaller area of the A loop surface. This limitation of the movements of the interloopings with respect to the A loop only becomes important at very high elongations. Additional interloopings will, however, be formed when loose chain ends are cross-linked.

If this schematic diagram is not too simple a representation of a three-dimensional network of polymer chains in thermal turmoil, one would expect the concentration of effective chains to equal the sum of a constant and the concentration calculated from the amount of curing agent. The constant represents the concentration of additional chains formed by entanglements. The data in Fig. 8 agree

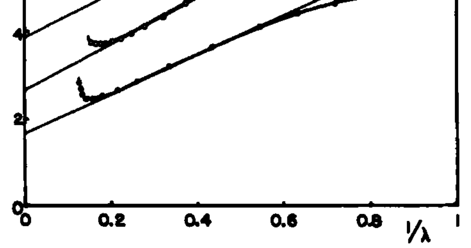

FIG. 10. Mooney-Rivlin curves of polybutadiene A cross-linked with azocarboxylate (DMDADC).

qualitatively with this expected relation. The slopes of the lines for the two series of samples cured with peroxide is somewhat more than the expected value of 1. The slopes of the sets of the polymers cured with azocarboxylate is less than unity. This may be due to the formation of a more complex network structure (see below); peroxides form cross-links of a single carbon bond, while those produced by azocarboxylate are 19 bonds long.

The entanglement concentrations represented by the intercepts is higher for the sets of polybutadiene vulcanizates than for natural rubber. It appears that small differences in the length of the cross-links and in the chemical nature or the stiffness of the polymer have a significant influence on the detailed arrangement of network meshes.

Medium Extensions

Some examples of the Mooney-Rivlin plots obtained with polybutadiene A vulcanizates are given in Fig. 10. The data do not agree with the continuum theory or with the statistical theory. As pointed out above, the observed elastic behavior is in accord with the sta-

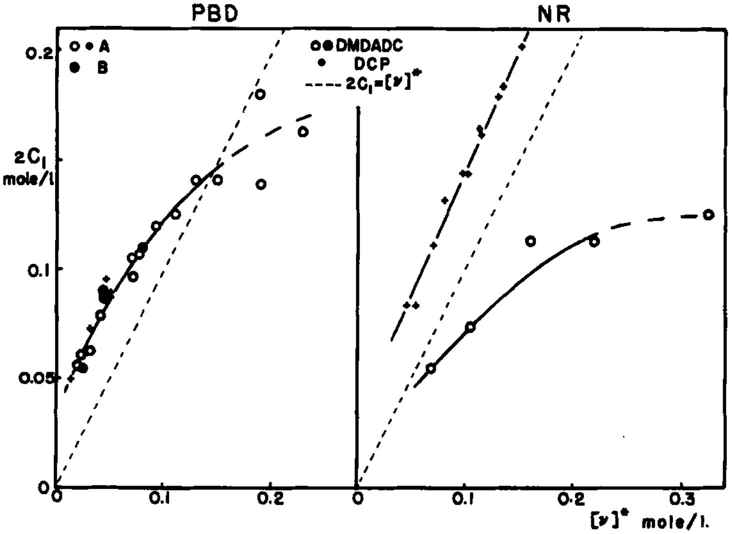

FIG. 11. Values of the parameter $2C_1$ at 25°C as a function of chain concentration $[\nu]^*$. The data for peroxide-cured natural rubber are from Bristow (*11*).

tistical theory at low elongations, but at higher extensions large deviations occur. To describe the observed elastic behavior straight lines have been drawn in plots such as Fig. 10 through the experimental points for elongations between about 70 and 4 to 500%. These lines are given by their intercepts $2C_1$ and slopes $2C_2$. Although these two parameters, suggested by the continuum theory, are used to characterize the elastic response of the samples at medium extensions, no adherence to this theory is implied. The term $2C_1$ [Eq. (1)] is usually identified with the corresponding term $[\nu]RT$ [Eq. (3)] of the statistical theory, although there is no theoretical justification for it. C_2 may be considered a measure of the deviation from statistical theory.

Values of $2C_1$ are plotted in Fig. 11 as a function of the chain concentration $[\nu]^*$ calculated from the amount of cross-linking agent used. The data show that there is a marked difference between $2C_1$ and $[\nu]^*$, and also that C_1 values depend on the chemical nature of the polymer and on the type of reaction used for cross-linking. Reliable values for C_1 and C_2 of peroxide cured polybutadiene can only be obtained at low cross-link densities because the tighter cross-linked samples break at relatively low elongations.

It follows from the definition of $2C_1$ that it is the value of the shear modulus at infinite extension on the assumption that this modulus is linearly related to the inverse extension ratio at medium and high elongations. Therefore, the significance of the hypothetical modulus $2C_1$ hinges on the validity of the assumption that the phenomenon, which causes the shear modulus to decrease with increasing elongation, is not in any way limited by the extension ratio. In other words, the significance of $2C_1$ depends on the type of phenomenon which gives rise to the C_2 term. This also follows from the observation (*13*) that negative values of C_1 have been found for some ethylene–propylene vulcanizates with high values of $2C_2$ (0.3 mole/liter). We therefore turn our attention first to the term C_2.

Values of $2C_2$ as a function of chemical chain concentration are shown in Fig. 12. It is seen that C_2 depends on this concentration, on the type of cross-linking agent, and on the nature of the polymer. In Table 1 a few approximate values of $2C_2$ are listed for a number of polymers. It is remarkable that C_2's of polybutadiene A are about 3 times higher than those of natural rubber and 20 times higher than those of polydimethylsiloxane.

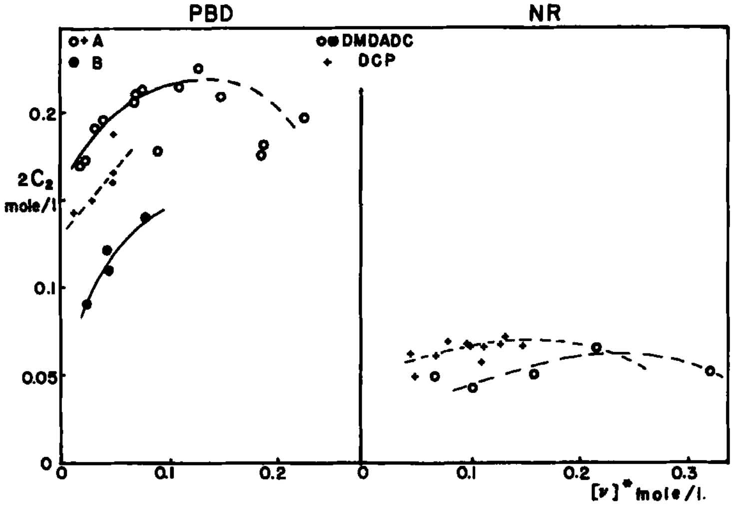

FIG. 12. Values of the parameter $2C_2$ at 25°C as a function of chain concentration $[\nu]^*$. The data for peroxide-cured natural rubber are from Bristow (*11*).

Comparison of polybutadienes A and B and of synthetic polyisoprene with natural rubber shows that even small differences in the chemical structure of the polymer are accompanied by noticeable differences in their C_2 values.

The term C_2 depends little on temperature. For polybutadiene A cured with azocarboxylate we found an increase of 6% over the temperature range from −20 to 40°C. Roe and Krigbaum (*16*)

TABLE 1

Approximate Values of $2C_2$ for Chain Concentrations between about 0.1 and 0.3 mole/liter

Polymer	$2C_2$: mole/liter, 25°C	Ref.
Polybutadiene A (93% *cis*-1,4; linear)	~0.21	This paper
Polybutadiene B (97% *cis*-1,4; slightly branched)	~0.15	This paper
Styrene–butadiene copolymer (emulsion)	0.13	(*14*)
Polyisoprene (92% *cis*-1,4)	0.08	(*11*)
Natural rubber	0.06	(*11*)
Butyl rubber	0.06	(*15*)
Polydimethylsiloxane	0.01	(*15*)

report an increase in C_2 of natural rubber of about 4% from 30 to 60°C. C_2 values of SBR vulcanizates (*10*) were found to be constant between 10 and 100°C. Smith and Frederick (9) reported recently that C_2 of butyl rubber is constant between −20 and 150°C, and the very small values of C_2 of silicone rubber are either constant or increase slightly in the wide temperature range −45 to 200°.

These data demonstrate that the phenomenon which gives rise to the C_2 term is not pure viscous. Nor is it solely an entropy-elastic phenomenon, since C_2 should then be proportional to the absolute temperature and an increase of 70% would be expected over the temperature range −20 to 150°C, which, at least for butyl rubber, is not observed.

From the data on the weak temperature dependence of C_2 rough estimates can be obtained of the energy and entropy components of this parameter. The contribution of energetic processes to C_2 is about 60% for polybutadiene, 50% for natural rubber, and 100% for butyl rubber. Because the statistical theory considers only entropic processes, and since C_2 is a measure of the deviation of the experimental from the theoretical elastic force, it is of interest to compare C_2 values with the energy contribution f_e to the total elastic force f. The ratio f_e/f can be determined experimentally from the temperature dependence of the stress and the force-extension relation. The results presented here have been calculated from the following equations:

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\delta f}{\delta T}\right)_{p,\lambda} + \alpha T \tag{4}$$

$$\frac{f_e}{f} = 1 - \frac{T}{2C_1^* + 2C_2^*\lambda^{-1}}\left[\left(\frac{\delta 2C_1^*}{\delta T}\right)_{p,\lambda} + \left(\frac{\delta 2C_2^*}{\delta T}\right)_{p,\lambda}\lambda^{-1}\right] + \alpha T \tag{5}$$

where α is the linear thermal expansion coefficient. The first of these equations, derived by Flory et al. (*17*), is based on the stress-strain relation of the molecular theory. This equation was used to allow a valid comparison with data on other polymers usually calculated with Eq. (4) or equivalent expressions. The second equation is derived from the *experimental* stress-strain relation and the assumption that both the C_1 term and the C_2 term contribution to the stress may be corrected for volume changes by (*17*)

$$(\delta f/\delta T)_{p,\lambda} = (\delta f/\delta T)_{V,1} + f\alpha$$

In the calculations of f_e/f the parameters $2C_1^*$ and $2C_2^*$ were taken to be the intercept and the slope of the tangent to the Mooney-Rivlin curves at the appropriate reciprocal extension ratio. The results calculated from this equation are considered to be more realistic than those from relation (4). The last term in Eqs. (4) and (5) is an approximation for the correction required by the volume change of the sample. Its value is relatively small—for polybutadiene 0.06 at 25°C.

The results for polybutadiene A are shown in Fig. 13. It can be seen that there is an appreciable difference between the sets of results calculated according to Eqs. (4) and (5). In both sets the ratio f_e/f is positive for extension ratios smaller than about 3, and it decreases with elongation. Comparable results have been reported by Crespi and Flisi (*18*) for a polybutadiene similar to our type B. The differences between the results obtained at 0° and at 25°C and those between specimens with chain concentrations of 0.072 and 0.129 mole/liter are smaller than the experimental error. Although the accuracy of the results at small deformations decreases rapidly with decreasing extension, the maximum in f_e/f is believed to be real.

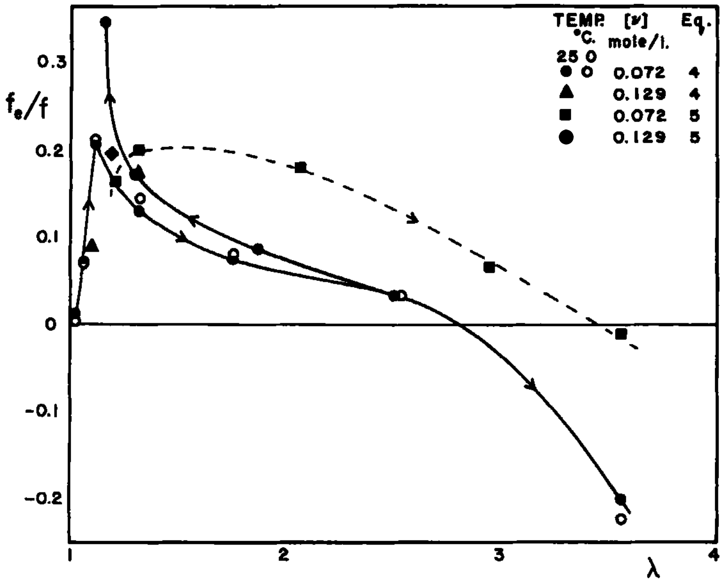

FIG. 13. Values of the ratio f_e/f as a function of extension ratio λ for polybutadiene A.

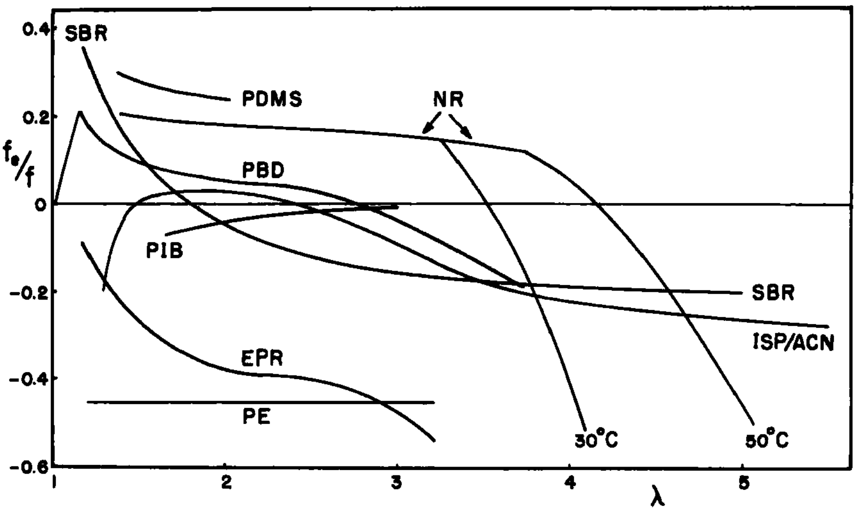

FIG. 14. Comparison of the dependence of f_e/f on extension ratio for various polymers. SBR, styrene-butadiene rubber (*19*), (see p. 780); PDMS, polydimethylsiloxane (*20*); NR, natural rubber (*21*); PBD, polybutadiene A (Fig. 13); PIB, butyl rubber (*22*); ISP/ACN, isoprene-acrylonitrile rubber (*23*); EPR, ethylene-propylene rubber (*24*); PE, polyethylene (*22*).

A comparison of these results with data of other polymers is made in Fig. 14. It is seen that the values of f_e/f vary greatly and that this ratio decreases with extension for most of the polymers.

Krigbaum and Roe (*25*) have pointed to a possible association between f_e/f and the C_2 term of the stress-strain relation. They note that the sign of C_2 is always positive and that f_e/f decreases with extension, irrespective of whether f_e/f is positive or negative. It is also noteworthy that f_e/f of rubber and SBR depends weakly on elongation at high extensions† and their C_2 values are independent of temperature, whereas for the other polymers f_e/f decreases with extension and C_2 varies somewhat with temperature. We may further point to the observation that at small elongations the slope of the Mooney-Rivlin curve of polybutadiene and the ratio f_e/f approach zero with decreasing deformation. Therefore, it seems worthwhile to further consider the energy contribution to the elastic force.

If this contribution arises from variation in energy with chain configuration, e.g., from energy barriers impeding rotation of bonds in the polymer backbone, then, according to the statistical theory, the

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† Smaller than those which induce stress crystallization.

following equation should hold:

$$f_e/f = T(d \ln \overline{r_0^2}/dT) \qquad (6)$$

where $\overline{r_0^2}$ is the average square end-to-end distance of free, undeformed polymer chains. It follows from this equation that the fractional energy contribution to the elastic force should be independent of deformation. Although this is clearly often not the case, it is nevertheless of interest to compare f_e/f with $Td \ln \overline{r_0^2}/dT$ measured by independent methods. Values of this last quantity can be obtained from the temperature dependence of dilute-solution viscosities. In general, the results of such measurements reported by different investigators do not agree well. Nevertheless, it seems probable that for some polymers average values of f_e/f are about equal to $Td \ln \overline{r_0^2}/dT$, as shown in Table 2 (ref. temp. 25°C). However, for other polymers, including polybutadiene, values of f_e/f have signs opposite to those of $d \ln \overline{r_0^2}/dT$. These discrepancies and the decrease of f_e/f with extension lead to the conclusion that configurational energy changes may contribute to the energy part of the force but they are not the only source.

The sharp decrease of f_e/f at high elongations of natural rubber is due to increasing stress crystallization, as Ciferri has shown. Polybutadiene will also crystallize on stretching at low temperatures, but the few experiments in which crystallization did occur ($\lambda = 3.6$, temp. < -10°C) have been discounted in calculating the reported f_e/f data. Nevertheless this ratio decreases markedly for polybutadiene and other amorphous polymers. X-ray photographs of butadiene–acrylonitrile, isoprene–acrylonitrile, styrene–butadiene, and ethylene–propylene copolymers show two-dimensional order at high extensions. This suggests that in these cases local interactions between segments of chains play a role. Such interactions

TABLE 2

Polymer	f_e/f	$T(d \ln \overline{r_0^2}/dT)$	Ref.
Polyethylene	-0.45	-0.41	(*22*,*26*)
Polyisobutylene	-0.05	-0.05	(*22*,*27*)
Polystyrene	0.14	0.16	(*28*)
Polydimethylsiloxane	0.26	0.24	(*20*)
Polybutene-1 (atactic)	0.21	<0	(*29*,*30*)
Polybutadiene	~ 0.1	-0.24	Fig. 13; (*31*)

will contribute to the C_2 term, as has been shown by Guth and James (*32*), and to a change of f_e/f on stretching; mutual attraction of chains leads to a decrease of this ratio. Attractive forces between chains of the acrylonitrile copolymers can be accounted for by the interaction of the dipoles of the nitrile groups. No such ready explanation is applicable to hydrocarbon polymers.

Interactions between chain segments is greatly reduced when the polymer network is swollen. The results reported for swollen networks of natural rubber (*21*), polydimethylsiloxane (*33*), polyethylene (*22*), and butyl rubber (*22*) (at small deformations) clearly indicate that f_e/f is unaffected by swelling, except for natural rubber at very high extensions, where solvent interferes with stress crystallization. These observations indicate that interaction of chain segments is not the major source of the energy contribution to the elastic force at low and medium extensions. At high elongations, however, interaction between chain segments may well contribute to f_e as has been demonstrated for stress-crystallizing polymers (*21*). Whether this is the case in our polybutadiene samples is difficult to verify, because swollen vulcanizates at high extensions break long before the time-consuming stress-temperature experiments can be completed.

It may be of significance to point out that various ethylene/propylene copolymers having $2C_2$ values ranging from 0.1 to 0.3 mole/liter vary greatly in the degree of two-dimensional order at high extensions evident from X-ray photographs. At present insufficient data are available to relate this degree of order to the value of the C_2 term or the dependence of f_e/f on elongation.

Entanglement Slippage

Let us now examine the relation between the parameters C_1 and C_2 and the chain concentration calculated from the stoichiometry of the vulcanization reactions. The high values of the shear modulus G at very small elongations have been ascribed to the large number of chain entanglements. The values of $2C_1$ are very much closer to the chain concentration. The difference $G - 2C_1$ is nearly constant. For our polybutadiene samples $G - 2C_1$ is about 0.04 mole/liter smaller than $2C_2$. This is the result of the initial curvature of the Mooney-Rivlin curve. For natural rubber $G - 2C_1$ differs little from $2C_2$. Since G and $2C_1$ are the shear modulus at zero and

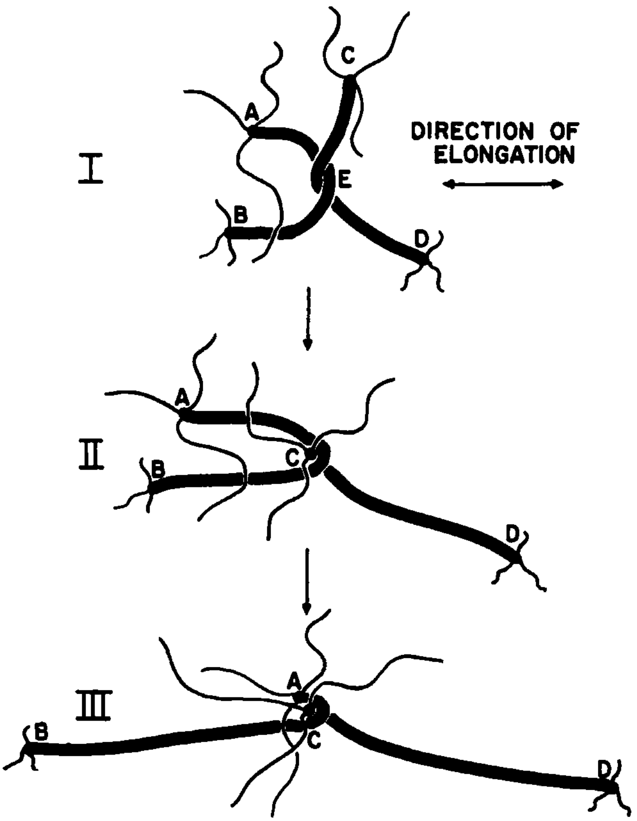

FIG. 15. Schematic diagram of entangled polymer molecules illustrating slippage of entanglements on elongation.

infinite elongations, respectively, we may, therefore, associate $G - 2C_1$ or $2C_2$ with the mechanism by which entanglements become ineffective on extending the sample from very small to very large elongations. Figure 15 illustrates such a mechanism schematically. The chains AB and CD are entangled at E. Initially the cross-link points A, B, C, and D are assumed to move approximately affine with the macroscopic dimensions of the sample. At small elongations (I) slippage of the chain AB through the entanglement with chain CD and vice versa is prevented by the local friction at E. The assembly reacts as a set of four chains: AE, BE, CE, and DE. On further elongation the relative increase in extension ratio of chain DE is larger than that of CE because the direction of DE is closer to the direction of elongation. The chain CE may actually contract rather than extend, depending on the sample elongation and on the angle between CE and the direction of elongation. Therefore, the difference in the forces exerted by the two parts of the chain CD on each other increases more than proportional to the extension ratio. If this increasingly larger difference overcomes the friction at E the chain DE drags CE through the entanglement until the other chains tied to CE by cross-link C obstruct further slippage (II). A similar process will occur at higher extensions for chains like AB. Because of the more symmetrical arrangement of AB with respect to the direction of elongation, friction will not be overcome until higher extensions are reached (III). Thus the number of chains of the original group of four is reduced to two.

This simple scheme must be modified when allowance is made for the nonaffinity of the cross-link movements. Nevertheless, the influence of a local frictional force at the entanglement point remains. Such friction opposes the slippage of chains not only on extension but also on contraction. Therefore, if on elongation a configuration of chains as in Fig. 15(III) has been formed, rearrangement to the configurations II and I on contraction will occur at smaller extension ratios than those necessary for the formation of these configurations. Local friction of slipping chains will, therefore, result in lower stress at equal strains on contraction than on elongation. Such differences in the stress-strain relation are indeed observed. The phenomenon is known as the Mullins' effect. It is most often recorded for black-filled rubbers, but it has been shown recently (*34*) that the effect results mainly from the properties of the rubber matrix and does not stem from polymer-black interaction.

The data reported here and many others in the literature are equilibrium data in the sense that the stress at a given deformation does not change with time. They do, however, refer to irreversible processes and are nonequilibrium data in the sense that the value of the stress at a given elongation depends on whether the sample was extended continuously to this elongation or was allowed to retract after being overextended, either mechanically or by swelling. This irreversibility, which has in general escaped the attention it deserves, is shown in the form of Mooney-Rivlin plots in Fig. 16. The slope of the initial part of the retraction curve ($2C_2'$) is smaller than that of the final part of the elongation curve ($2C_2$) and depends on

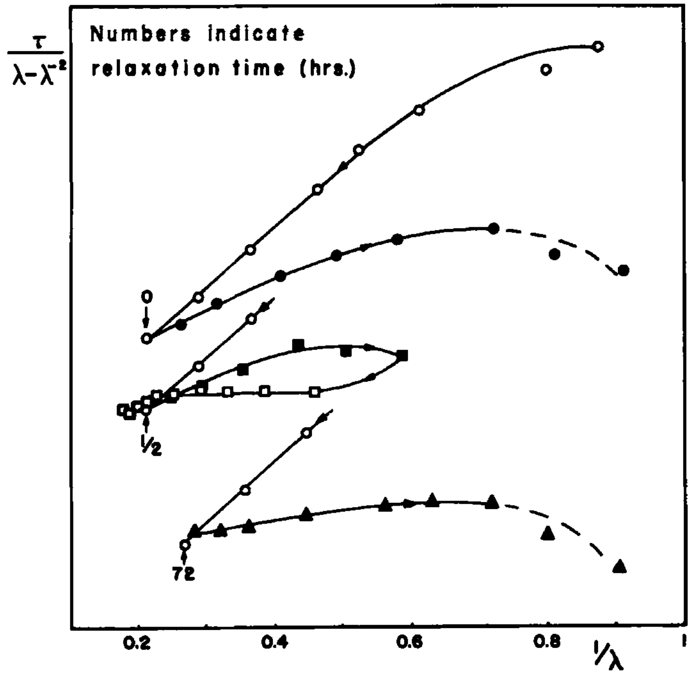

FIG. 16. Mooney-Rivlin curves on elongation and contraction of a sample of polybutadiene A ($[\nu]^* = 0.05$ mole/liter). Two of the sets of curves have been shifted along the ordinate axis for clarity.

the relaxation time allowed at the turning point. The ratio C_2'/C_2 is 0.51, 0.45, and 0.17 after relaxation times of 0, ½, and 72 hr, respectively. Elongation appears to have changed the network such that on retraction the deviation from statistical theory is appreciably less. The more time is allowed for entanglements to slip and to form tightly intertwined knots, the more the rubber resembles the network model of independently reacting chains underlying the statistical theory. That there is a change in the arrangement of chains in the network can also be seen from the stress-strain behavior on reelongation (Fig. 16, □), which agrees well with theory between 200 and 450% elongation. The mechanism described is compatible with the observation (35) that on reelongation of natural rubber the stress-strain relation follows approximately the contraction curve up to the previous maximum elongation and then follows the original extension curve.

These results are at least qualitatively in agreement with the schematic picture of slipping chains given above. If this slipping mechanism can be associated with C_2 one might expect that this parameter is less than normal when disentangled polymer is vulcanized. Such reactions were carried out by putting cold preshaped mixtures of polymer and azocarboxylate along *one* side of the cavity of a preheated mold which was quickly closed in a warm press (60°C). Thus the polymer was vulcanized shortly after it was, at least partially, disentangled by flow. The polymer chosen was the slightly branched polybutadiene B, whose short time relaxation is much less than that of the linear polybutadiene A. The degree of anisotropy of the samples is expressed by the ratio S_w/S_e, where S_e and S_w are the linear swelling ratio in the direction of elongation and perpendicular to this direction, respectively.

Table 3 shows that the $2C_2$ values of the anisotropic samples are appreciably less than that of the isotropic specimen. Because this decrease in $2C_2$ is independent of whether the sample is elongated in the same direction as that of the flow prior to vulcanization, or perpendicular to the flow direction, it is not a result of preorientation of the polymer chains but is attributed to the decrease of entanglement density and/or slippage of entanglements to form intertwined knots which are consolidated by the subsequent vulcanization reaction. To obtain reproducible stress-strain data it is, therefore, necessary to cure polymers in a relaxed condition.

If the original polymer is not entangled, vulcanizates formed from it should have no C_2 term. This has indeed been observed. Kraus and Moczvgemba (*36*) have vulcanized polybutadiene with a molecular weight below the entanglement molecular weight of the raw polymer as determined from the melt-viscosity dependence on molecular weight. Curing was achieved by reaction with the carboxy

TABLE 3

Values of the Parameter $2C_2$ for Samples of Polybutadiene B of Various Degrees of Anisotropy

Direction of flow and direction of elongation	Perpendicular			No flow	Parallel		
S_w/S_e, in benzene	0.88	0.92	0.94	1.00	1.02	1.11	1.59
$2C_2$, moles/liter	0.07	0.06	0.08	0.11	0.05	0.03	<0

end groups of the polymer. The C_2 values of these vulcanizates were either very small or zero.

It can further be concluded that C_2 of swollen samples (C_{2s}) should be smaller than C_2 of dry specimen (C_{2d}) because during the swelling process, also, entanglements will slip to form knots. Therefore, less entanglements can slip during subsequent elongation of the swollen specimen. This argument has been developed in a quantitative form which yields $C_{2s} = C_{2d}v_r^{4/3}$, in which v_r is the volume fraction of polymer in the swollen rubber (37). Earlier this relation had been found empirically.

If the C_2 term is associated with a change in network topography on deformation, as these considerations suggest, then C_2 should depend mainly on the geometric details of the network structure, not on the nature of the polymer. We do, however, observe a spread in C_2 values for various polymers. We may speculate that this variation results from either or both of two factors:

1. Differences in the configurations of the uncured polymer molecules which would affect their end-to-end distance. However, several theories concerning properties of polymer solutions and based on a statistical treatment have been confirmed by experimental results. Therefore, differences in configuration between polymers would refer to bulk polymer only, and not to solutions of these polymers. The main factor, neglected by the statistical theory, influencing the end-to-end distance of bulk polymer is the excluded volume. It does not seem plausible that this correction could account for the large differences between polymers observed. Furthermore, McQuarrie and Shen (38) have recently calculated the effect of intrachain excluded volume on elasticity from Edward's distribution functions of end-to-end distances (39). The effect results in a negative C_2 term in the Mooney-Rivlin curve, contrary to observation.

2. Differences in the rearrangement of chain configurations during the vulcanization reaction. Such differences are expressed by the term $\overline{r_n^2}$ in Eq. (3). The gradual introduction of restraints on the thermal motion of the polymer molecules during cure affects the configurations of the chains in the resulting network. This effect, which depends mainly on the rate of relaxation of the polymer molecules relative to the rate of the vulcanization reaction, may account for the sensitive dependence of C_2 on the chemical constitution of

the polymer and on the degree of branching. In this connection it is worth mentioning that our polybutadiene A samples relax fast; after extension to 200% elongation and a 10-min rest period the stress-strain curve of reextension differs little from the original extension curve. Polybutadiene B relaxes much slower.

It follows furthermore that the term $2C_1$, although largely governed by the cross-link density, depends also on factors reflecting the detailed structure of the network. Cross-link densities are often calculated from swelling data and the polymer-solvent interaction parameter μ. The value of μ is determined from a relation based on the statistical theory with the assumption that $2C_1$ is equal to the chain density. Since the degree of entanglement slippage depends on the swelling ratio, which in turn depends on cross-link density, it is perhaps not surprising that experimental values of μ have been reported which vary with cross-link density, contrary to what one would expect from the physical significance of this parameter. Therefore, cross-link densities calculated from swelling data and μ should be regarded with reservation.

High Deformations

In the Gaussian molecular theory of elasticity the force acting on a model chain is proportional to its end-to-end distance. To further extend polymer chains, however, which are stretched to lengths approaching their contour lengths, a rapidly increasing force is required. At high elongations the fraction of the network chains which approach the limit of their extensibility increases. Ciferri (*21*) and others have shown that this is the reason for the sharp increase in the shear stress as shown in Mooney-Rivlin curves of amorphous rubbers at high elongations. Treloar (*40*) and Smith et al. (*41*) have refined the molecular theory taking the finite extensibility of chains into account. The stress-strain relations developed in these theories, which predict the upturn in the Mooney-Rivlin curves, contain a parameter: the length of the statistical link. Values for this length can be obtained from the position of the upturn. For natural rubber Morris (*42*) has calculated the contribution of finite extensibility to the C_1 term of the force over the whole stress-strain curve. He found a small but significant contribution. From similar calculations for vulcanizates of polybutadiene A with chain concentrations of 0.2 mole/liter, we find that the fraction of the C_1 term of the force due to finite extensibility is 2.5 and 5% at 0 and 100% elongation, respectively. We may conclude from these data that even at low elongations a small but significant fraction of the network chains is highly extended. These chains exert strong, local forces on their entanglement points and on the cross-links at their ends, thus promoting the slippage of these entanglements and those of the chains attached to their ends.

The number of monomer units per statistical link, q, of polybutadiene, calculated from the position of the upturn, is compared in Table 4 with values for q of natural rubber and with those obtained by other methods.

TABLE 4

Values of q, the Number of Monomer Units per Statistical Link

Polymer	Method Stress-strain	Light scattering	Viscosity of moderately concentrated solutions
Polybutadiene A	2.4	2.4[a]	2.1
Polybutadiene B	1.8	1.4[a]	1.2
Natural rubber	4.3[b]	3–6[c]	4–6[d]

[a] Ref. (*43*).
[b] Ref. (*42*).
[c] Ref. (*44*).
[d] Ref. (*45*).

The agreement of these values is better than expected for results from such diverse methods. It seems justified to consider polybutadiene the more flexible polymer, in agreement with what may be expected from its low glass transition temperature (A, −108°; B, −114°; NR, −70°C) and its high resilience (ball rebound at 25°C in vacuum: A, 97%; NR, 85%).

From these q values and others reported in the literature we calculate approximate values of the number of polymer backbone atoms in the statistical link Q, and compare Q with $2C_2$ values in Table 5.

Even though these values are only approximate, it is clear that there is no direct relation between Q and C_2. This lack of correla-

TABLE 5

Approximate Values of Q, the Number of Backbone Atoms per Statistical Link and Approximate Values of $2C_2$ of the Mooney-Rivlin Equation

Polymer	Q	$2C_2$: mole/liter, 25°C
Polybutadiene A	10	0.21
Polybutadiene B	6	0.15
Natural rubber	15–25	0.06
Butyl rubber[a]	16	0.06
Polydimethylsiloxane[a]	10	0.01

[a] Ref. (*46*).

tion agrees with the notion that differences in the configurations of the uncured polymer are not the reason for the variation in C_2 values. A comparison of the data of both polybutadienes may be taken to support the suggestion that the C_2 value is determined by the rate of relaxation of the polymer molecules during the network formation on cure. Branched polybutadiene B has distinctly lower C_2 and Q values than linear polybutadiene A. In a vulcanizate branch points of long-chain branches are indistinguishable from cross-links. It is envisaged that the lower C_2 values of B result from the low relaxation rate during the vulcanization reaction of the

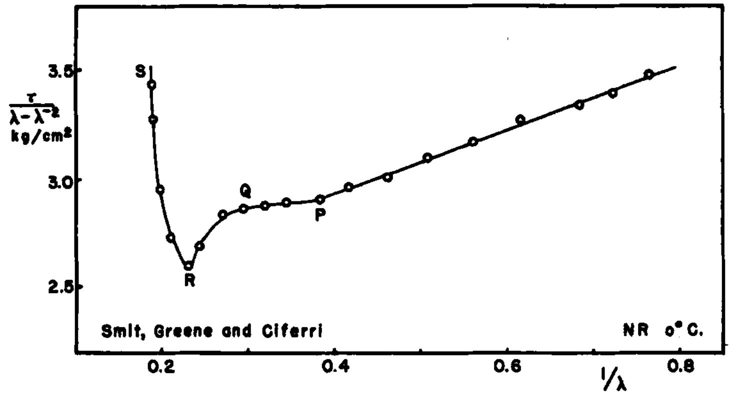

FIG. 17. Example of Mooney-Rivlin plot demonstrating the influence of finite extensibility of network chains and stress crystallization. Data from Ref. (*21*) for natural rubber at 0°C, $[\nu]^* \sim 0.09$ mole/liter.

polymer B due to its branched structure and in spite of its high flexibility.

Smith et al. (*21*) have made an extensive study of the upturn in the Mooney-Rivlin curve of natural rubber. Some of their results are reproduced in Fig. 17. It was shown that the first deviation from the linear portion of the Mooney-Rivlin curve (P) is associated with the non-Gaussian behavior of that fraction of the chains which approach the limit of their extensibility. This fraction mainly consists of the *short* chains of the network, which have been elongated further than the sample. Hence the shear modulus decreases less (PQ) than in the linear portion of the MR curve. As a result of the stiffening of these short chains, neighboring chains attached by cross-links also become overstressed, and they orient more than the average network chain. This process is illustrated in Fig. 18, in which a portion of the network is represented in two dimensions at various stages of elongation. Of the very many paths that may be traced between planes A and B following chains from cross-link to cross-link, a few are much shorter than the average. Short individual chains of these short circuits will become fully extended at relatively low elongations. One such chain (J) is shown in section CD and the effect of further extension on the stretching and orientation of

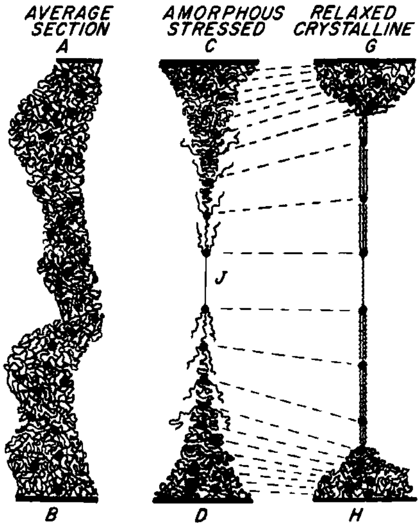

FIG. 18. Shortest-paths sections of extended rubber networks.

chains attached to J is illustrated in section GH. If the polymer stress-crystallizes, the chains extending from either end of J lose some of their kinetic energy as heat of crystallization and relax until the local excess of stresses has been dissipated. This relaxation results in a decrease in the shear modulus (QR in Fig. 17) and the highly extended parts of the network are protected from further stress concentration by crystallite formation.

On the other hand, there are three reasons why the shear modulus should increase:

1. The fraction of chains approaching their extensibility limits increases with elongation.
2. The number of elastically effective chains increases, owing to incorporation of segments of chains into crystallites.
3. The formation of a solid (crystalline) phase requires the amorphous portion of the network to deform more than the specimen.

It appears that initially these three effects do not compensate for the stress relaxation due to crystallization (QR). The steep ascent of the Mooney-Rivlin curve (RS) shows that on further elongation the effects of the three phenomena mentioned above override stress relaxation. Since crystallization is a temperature-sensitive rate process, the detailed shape of the Mooney-Rivlin curve depends on rate of extension and on temperature of the sample.

This description of the processes occurring at high extensions of stress-crystallizing rubbers has mainly been developed by Smith et al. (*21*) and by Buckler (*47*). The experimental results obtained by the former authors amply support it.

Several investigators have noted in the past a similarity between the effect of crystallization in natural rubber gum stocks and the effect of carbon black in amorphous rubbers. It is of interest to speculate whether a protective mechanism similar to the one outlined above could be provided by carbon black reinforcement of amorphous rubber networks. Relaxed, coiled chains can offer only isolated points of contact with carbon black surfaces. However, if a particular chain J (Fig. 18) is highly stressed during the early stages of extension of a specimen, it will be unravelled and elongated. To a lesser degree chains extending from each end of J into the surrounding network will also become elongated. As a result, the surfaces of carbon black particles will become accessible to an increasing number of links of these particular, stressed chains.

Adsorption of polymer chains onto black surfaces occurs when the attractive energy between them is larger than the product of absolute temperature and the decrease in chain entropy associated with adsorption. Since the entropy of the highly stressed chains has already been reduced on elongation, further loss of entropy required for adsorption is less. Hence these particular chains tend to become adsorbed. The predominant effect of increased accessibility of black surface and of enhanced probability of adsorption of chains will be to dissipate the kinetic energy of these particular chain segments in the form of heat of adsorption. If this hypothesis is correct, the mechanism of reinforcement by carbon black is similar to that postulated for the effect of crystallization. In other words, carbon black may induce relaxation of overstressed chains by removal of their kinetic energy, which postpones rupture and permits other parts of the network to become elongated to carry the load.

Because the end-to-end length of a partially elongated chain can be several times the diameter of a carbon black particle, protection against rupture of segment J by this means can be provided by carbon black particles situated at some distance from segment J. By a mechanism of this sort, the small proportion of prematurely elongated chains may be protected from rupture, and tearing of the specimen avoided, while further extension of the specimen permits the average chains to become elongated to carry the load.

A qualitative difference exists between black reinforcement and crystallization. To protect the few overstressed chains in a natural rubber gum vulcanizate, up to 30% of the total rubber becomes crystallized on extension. This produces changes in internal energy of the whole specimen; hence the ratio f_e/f decreases rapidly at high elongations (see Fig. 14). In the case of carbon black reinforcement, only the internal energy of the overstressed chains will be affected, and these probably constitute too small a proportion of the total specimen to give rise to detectable changes in f_e/f for the whole specimen.

One of the reasons mentioned above for a higher shear modulus can be evaluated quantitatively. In the presence of black or crystallites the true extension λ^* of the network is greater than the extension λ of the specimen, to compensate for the lack of extension of the solid phase. According to Bueche (*48*), the relation between λ^* and λ is given by

$$\lambda^* = (\lambda - v_f^{1/3})/(1 - v_f^{1/3}) \qquad (7)$$

This relation has been derived on the basis of geometric considerations only, and does not contain any adjustable parameters. The effect of a solid phase on internal extension is large; for instance, for a black loading of 50 phr ($v_f = 0.20$), $\lambda^* = 6$ when $\lambda = 3$. Some experimental data are in agreement with Eq. (7). For example, the values of f_e/f for SBR in Fig. 14 have been calculated from the results of a comprehansive study by Stearns and Johnson (*19*) of the stress-strain and thermodynamic functions of SBR reinforced with different amounts of SRF black. The original data are shown on the left of Fig. 19. If these are corrected for the filler effect by Eq. (7) and plotted against λ^*, the data for all compounds, including gum stock, fall on the same curve (Fig. 19, right). In other words, the stress-strain properties of vulcanized, amorphous rubbers reinforced with carbon black are the same as for the corresponding gum stocks, except that the carbon black has made it possible to extend the rubber to higher elongations before rupture occurs.

Another application of Eq. (7) is shown in Fig. 20. These data have been calculated from results obtained by Holt and McPherson (*49*). In the top section the volume change of natural rubber gum and

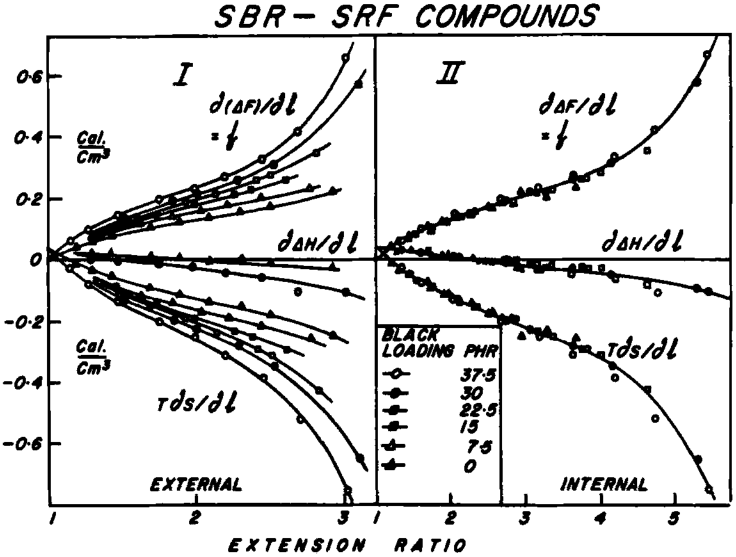

FIG. 19. Thermodynamic functions of styrene–butadiene rubber with varying amounts of SRF black as a function of external and of internal extension ratio. [Data from Ref. (*19*).]

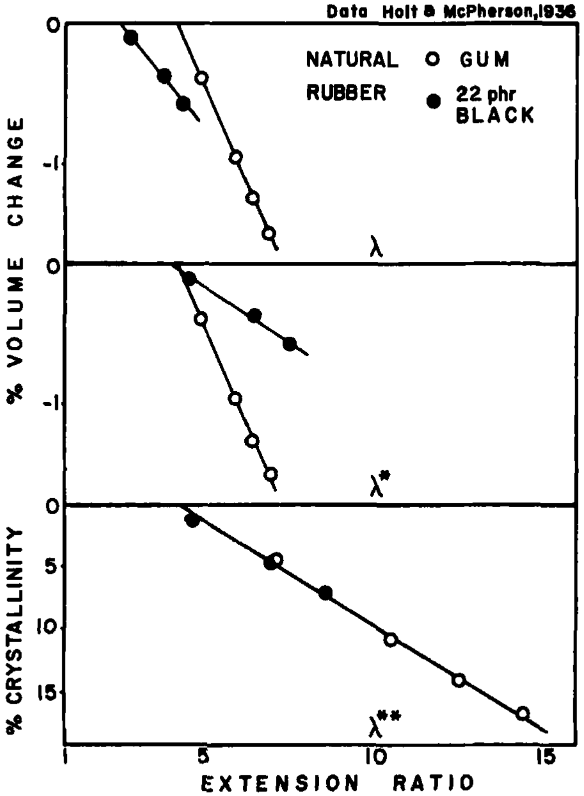

FIG. 20. Degree of crystallinity developed in natural rubber gum and black reinforced vulcanizates as a function of extension ratio. [Data from Ref. (*49*).]

black reinforced vulcanizates is shown as a function of specimen elongation. The onset of shrinkage of the sample due to stress crystallization is seen to occur at different elongations. In the middle section the contraction is plotted against internal extension ratio λ^* calculated from Eq. (7) and the volume fraction of the black. Crystallization sets in at the same internal elongation for the filled and the gum vulcanizates. If now the volume fraction of the crystalline phase is calculated from the contraction of the specimen a new internal extension ratio λ^{**} can be computed, taking into account the volume fraction of the black and/or the crystallites. The results plotted in the bottom section of the figure show that there is no difference between filled and gum compounds. In other cases differences in deformation-dependent properties between filled and unfilled compounds do not completely disappear when these properties are compared on the basis of internal elongation. This could in part be due to cavitation, especially with surface-inactive fillers.

Other investigators have used different relations between internal and external extension ratios. Mullins and Tobin (*50*), for example, have found that the equation

$$(\lambda^* - 1)/(\lambda - 1) = 1 + av_f + bv_f^2 \qquad (a \text{ and } b \text{ are constants}) \qquad (8)$$

is applicable to natural rubber vulcanizates reinforced with varying amounts of carbon black. Relations (7) and (8) differ appreciably, particularly at low values of v_f. Which factors govern the applicability of these two equations remains to be established. It is appropriate to note that in the development of relation (8) it is tacitly assumed that there is no flow of the rubber in contact with the surface of the filler particles past this surface, while no such assumption is made in deriving Eq. (7). The difference between the two relations may therefore be associated with the absence or presence of chemical bonding of rubber to filler.

It may also be expected that chemical bonding of chains to particles will result in a wider distribution of deformations of individual chains than when the adsorption is physical, i.e., a dynamic equilibrium between adsorption and desorption. Such an equilibrium permits displacement of whole chains with respect to particle surface, impossible when the rubber is chemically bonded to the particle. Because of the nonlinear relation between stress and strain, the averaging method expressed in Eq. (7) may be adequate for one compound and not quite satisfactory for another.

Over the last decades significant advances have been made in the study of the technologically important property of failure. The viscous and elastic contributions to the failure stress have been separated. A master stress-strain curve has been constructed from appropriately reduced failure data of a variety of amorphous polymers, cross-linked to various degrees. It is, however, not understood why some amorphous polymers break at low elongations and others at high extensions. It seems probable that variations in network topography must be considered in the search for an answer to this question.

It has been described in the previous section how the *short* chains of a network are protected from premature failure in stress-crystallizing and black reinforced polymers. No protective mechanism of this kind operates for amorphous gum vulcanizates. The degree to which short network chains become overstressed is determined by the molecular-weight distribution of the chains, the functionality of the cross-links, and the length of the cross-links. The distribution is usually assumed to be a Gaussian one. At high elongations the functionality depends to a large extent on the original entanglement density, since the entanglements have then slipped toward the cross-links, forming tightly intertwined knots with high functionality. The higher its functionality the more affine is the displacement of a cross-link knot. At high extensions the knots will yield little to the pull of short chains, which have reached the limit of their extensibility. Hence short chains will break at relatively low elongations. One might, therefore, expect the elongation at break to decrease with increasing entanglement concentration, as measured by the C_2 term of the Mooney-Rivlin relation.

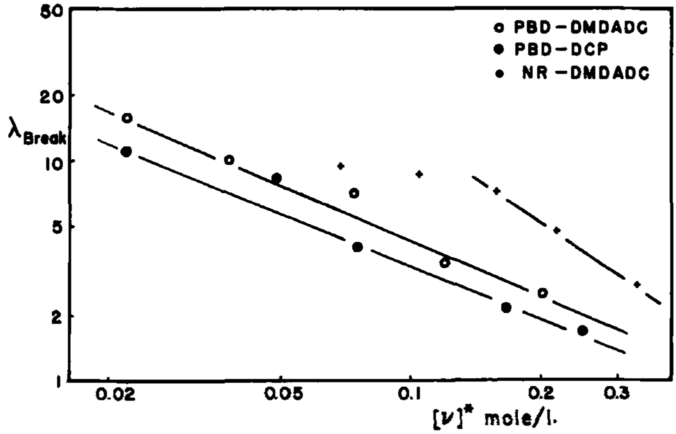

FIG. 21. Extension ratio at break as a function of chain concentration for polybutadiene (PBD) and natural rubber (NR) cross-linked with azocarboxylate (DMDADC) and dicumylperoxide (DCP).

The pertinent data for our vulcanizates are shown in Fig. 21, in which the maxima each of some 20 values of the elongation at break are plotted as a function of the chemical chain concentration. The natural rubber samples were broken at 55°C to prevent stress crystallization, which at this temperature sets in at about 600% elongation. It is seen that the polybutadiene samples which have the higher C_2 values break earlier than the natural rubber specimen. The influence of the length of the cross-links can be judged by comparing peroxide-cured and azocarboxylate-cured vulcanizates. Networks with unyielding single-bond cross-links formed by peroxide vulcanization break easier than those with cross-links consisting of 18-atom chains. These data are in accord with the suggested relation between network topography and sample failure.

CONCLUSIONS

The stress-elongation relations of *cis*-1,4 polybutadiene and of natural rubber are not in accord with the Mooney-Rivlin theory or with the statistical theory of elasticity.

At very small elongations both polymers behave in agreement with the statistical theory but the initial shear modulus is much larger than that calculated from the chemistry of the vulcanization reaction.

At larger deformations polybutadiene deviates much more from the statistical theory than does natural rubber.

There is no relation between the degree of deviation and the glass transition temperature or the chain stiffness of the polymer. Therefore, this deviation is not due to viscous effects. There is some indication that the deviation is associated with the rate of relaxation during the vulcanization reaction.

The observed elastic behavior is consistent with entrapment of entanglements during the vulcanization reaction and partial slippage of the entanglements during elongation.

The energy contribution to the elastic force (f_e) of polybutadiene varies between 20% at $\lambda \sim 1.2$ and zero or negative values at $\lambda > 3$.

The fraction f_e decreases with increasing λ for a variety of polymers including polybutadiene. Therefore, configurational energy changes are at least not the *only* source contributing to f_e.

Preferential adsorption onto carbon black particles of short network chains which become overstressed at high deformations probably contributes appreciably to the reinforcing effect of blacks.

The relation between extension of a filled sample and that of the elastomer matrix derived by Bueche is applicable to some systems.

Network topography has an influence on the ultimate properties of vulcanizates. Polybutadiene samples in which the cross-links are single bonds break at lower elongation than those with equal concentrations of cross-links consisting of 18-atom chains.

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REFERENCES

1. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
2. R. S. Rivlin, *Phil. Trans. Roy. Soc. (London)*, **241A**, 379 (1948).
3. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Clarendon Press, Oxford, 1958, p. 115.
4. P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).
5. B. M. E. van der Hoff, J. F. Henderson, and R. M. B. Small, *Rubber Plastics Age*, **46**, 821 (1965).
6. L. Mullins and W. F. Watson, *J. Appl. Polymer Sci.*, **1**, 245 (1959).
7. P. J. Flory, N. Rabjohn, and M. C. Shaffer, *J. Polymer Sci.*, **4**, 225 (1949).
8. B. M. E. van der Hoff, *Ind. Eng. Chem. Prod. Res. Develop.*, **2**, 273 (1963).
9. T. L. Smith and J. E. Frederick, *J. Appl. Phys.*, **36**, 2996 (1965).
10. T. L. Smith, private communication, 1963.
11. G. M. Bristow, *J. Appl. Polymer Sci.*, **9**, 1571 (1965).
12. L. C. Case and R. V. Wargin, *Makromol. Chem.*, **77**, 172 (1964).
13. J. R. Dunn, private communication, 1964.
14. Calculated from data published by T. L. Smith, *Trans. Soc. Rheology*, **6**, 61 (1962).
15. T. L. Smith, to be published in *J. Polymer Sci.*
16. R.-J. Roe and W. R. Krigbaum, *J. Polymer Sci.*, **61**, 167 (1962).
17. P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polymer Sci.*, **45**, 235 (1960).
18. G. Crespi and U. Flisi, *Makromol. Chem.*, **60**, 191 (1963). The values of $d \ln \overline{r_0^2}/dT$ for $\alpha = 1.48$ reported in Table 2 of this paper are in error. The correct values for 293°, 313° and 333°K are: 0.33; 0.26 and 0.19×10^{-3} respectively (Flisi, private communication, 1965).
19. R. S. Stearns and B. L. Johnson, *Ind. Eng. Chem.*, **43**, 146 (1951).
20. J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **86**, 138 (1964).
21. K. J. Smith, A. Greene, and A. Ciferri, *Kolloid-Z.*, **194**, 49 (1964).
22. A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).
23. Data kindly made available by S. K. Mukherjee of this laboratory.
24. G. Natta, G. Crespi, and U. Flisi, *J. Polymer Sci.*, **A1**, 3569 (1963).
25. W. R. Krigbaum and R.-J. Roe, *Rubber Chem. Technol.*, **38**, 1039 (1965).

26. P. J. Flory, A. Ciferri, and R. Chiang, *J. Am. Chem. Soc.*, **83**, 1023 (1961).
27. U. Bianchi, E. Patrone, and M. Dalpiaz, *Makromol. Chem.*, **84**, 230 (1965).
28. T. A. Orifino and A. Ciferri, *J. Phys. Chem.*, **68**, 3136 (1964).
29. J. E. Mark and P. J. Flory, *J. Phys. Chem.*, **67**, 1396 (1963).
30. F. Danusso, G. Moraglio, and G. Gianotti, *Ist. Lombardo R. Sci.*, **A94**, 566 (1960).
31. G. Moraglio, *European Polymer J.*, **1**, 103 (1965).
32. E. Guth and H. M. James, *Proceedings of the Third Rubber Technology Conference, London,* 1954, p. 368.
33. A. Ciferri, *Trans. Faraday Soc.*, **57**, 846 (1961).
34. J. A. C. Harwood, L. Mullins, and A. R. Payne, *J. Appl. Polymer Sci.*, **9**, 3011 (1965).
35. L. Mullins, *J. Rubber Res.*, **16**, 275 (1947).
36. G. Kraus and G. A. Moczvgemba, *J. Polymer Sci.*, **A2**, 277 (1964).
37. B. M. E. van der Hoff, *Polymer*, **6**, 397 (1965).
38. D. A. McQuarrie and M. C. Shen, paper presented at the *American Chemical Society Western Regional Meeting*, Los Angeles, Nov. 1965.
39. S. F. Edwards, *Proc. Phys. Soc. (London)*, **85**, 613 (1965).
40. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Clarendon Press, Oxford, 1958.
41. K. J. Smith, A. Ciferri, and J. J. Hermans, *J. Polymer Sci.*, **A2**, 1025 (1964).
42. M. C. Morris, *J. Appl. Polymer Sci.*, **8**, 545 (1964).
43. Data kindly made available by R. M. B. Small of this laboratory.
44. G. M. Bristow, *J. Polymer Sci.*, **A1**, 2261 (1963).
45. C. F. Cornet, *Polymer*, **6**, 373 (1965).
46. V. N. Tsvetkov, *Zh. Vses. Khim. Obshchestva im D. I. Mendeleeva*, **6**, 428 (1961); *Rubber Chem. Technol.*, **36**, 337 (1963).
47. E. J. Buckler, *Rev. Gen. Caoutchouc*, 41, 1801 (1964); *Rubber Age*, **96**, 238 (1964).
48. F. Bueche, *J. Appl. Polymer Sci.*, **4**, 107 (1960).
49. W. L. Holt and A. T. McPherson, *J. Res. Natl. Bur. Std.*, **17**, 657 (1936).
50. L. Mullins and N. R. Tobin, *J. Appl. Polymer Sci.*, **9**, 2993 (1965).

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Zusammenfassung

Die Theorie der Elastizität polymerer Strukturen hat sich in zwei Richtungen hin entwickelt. Die phänomenologische Richtung führte zu der Mooney-Rivlin Beziehung zwischen Spannung und Streckung bei uniaxialer Streckung. Die statistische Theorie der Elastizität auf der Grundlage eines Modells für polymere Moleküle sagte eine ähnliche Beziehung voraus, wobei eine der Konstanten den Wert null annimmt. Die tatsächlichen elastischen Eigenschaften von Gummi stimmen mit keiner der beiden Theorien voll überein.

Die hier berichteten experimentellen Befunde wurden mit quantitativ vulkanisiertem Polybutadien und Polyisopren erhalten. Diese Daten können als nahe dem Gleichgewicht liegende Resulate angesehen werden, da eine cyclische Spannungsfolge angewendet wurde wodurch zum grössten Teil der Einfluss von langperiodigem Kriechen eliminert wird. Die Abhängigkeit des anfänglichen Moduls und der Parameter der Mooney-Rivlin Beziehung von der chemischen Zusammensetzung und dem Verzweigungsgrad des Polymeren, der Art der Vernetzungen und der Temperatur wurde untersucht. Eine mögliche Beziehung zwischen der Energiekomponente der elastischen Kraft und einem der Parameter wird diskutiert.

Diese Ergebnisse als auch jene der Literatur beziehen sich auf irreversible Prozesse. Es wird angenommen, dass diese Irreversibilität auf Reibung beruht, die beim Gleiten von Kettenknäuel entsteht. Dieser Mechanismus steht in Einklang mit den beobachteten Abhängigkeiten. Es wurde geschlossen, dass die Änderung der elastischen Eigenschaften mit der Elongation auf Änderungen in der Topographie der Netzstruktur zurückzuführen sind.

Topologische Veränderungen bei vulkanisierten Netzstrukturen wurden bei sehr grossen Elongationen beobachtet. Auf Ähnlichkeiten zwischen der Strukturverstärkung durch Spannungskristallisation und durch Russzusatz wird hingewiesen. Der durch Russ hervorgerufene Effekt wird hauptsächlich zurückgeführt auf die bevorzugte Adsorption an den Russpartikeln von kurzen Ketten die bei hohen Deformationen überbeansprucht werden. Durch Adsorption wird die kinetische Energie dieser Kettenmoleküle als Adsorptionswärme abgeführt.

Weiterhin werden Beispiele angeführt für die Anwendung von Bueche's Beziehung zwischen der Dehnung der Probe und der elastomern Matrix eines gefüllten Vulkanisats. Diese Gleichung weicht von der auf Einstein's Beziehung für die Viskosität von Suspensionen beruhenden ab. Die letzere konnte im Falle anderer gefüllter Gummi angewendet werden. Der Unterschied zwischen den beiden Beziehungen dürfte mit der Anwesenheit oder Abwesenheit von chemischen Bindungen zwischen Elastomerem und Füllmaterial in Zusammenhang stehen.

Die Topographie der Struktur hat Einfluss auf die endgültigen Eigenschaften des Vulkanisats. Polybutadienproben, in welchen die Vernetzungen einfache Bindungen sind, brechen bei geringerer Elongation auf als solche mit gleichem Vernetzungsgrad wobei die Vernetzungen aus Ketten aus 18 Atomen bestehen.

Résumé

La théorie de l'élasticité du reseau macromoléculaire a été developpé dans deux sens. L'approche phénomènologique conduit à la relation de Mooney-Rivlin entre la contrainte et le taux d'extension pour l'extension uniaxiale. La théorie statistique d'élasticité, basée sur un modèle des molécules macromoléculaires, prévoit une rélation analogue avec une desconstantes zero. Les propriétés réelles du caoutchouc ne s'accordent pas complètement avec l'une ou l'autre théorie.

On fait un rapport sur les résultats expérimentaux obtenus avec des polybutadiènes et des polyisoprènes recuites quantitativement. Ces données représentent des résultats prèsque de l'équilibre par l'usage d'une série cyclique de contrainte, qui élimine largement l'influence du rampement prolongé. La dépendance du module et des paramètres de la relation de Mooney-Rivlin de la nature chimique et du degré de branchement du polymère, du type de réticulation et de la température a été étudieé. Une relation possible entre le composant d'énergie de la force élastique avec l'un de paramètres est discutée.

Ces résultats et ceux de la litérature s'appliquent aux processus irreversibles. On propose que cette irreversibilité résulte de la friction qui accompagne la disjonction des chaînes entremelées. Ce mécanisme est en accord avec les relations observées. On conclu que la variation des proprietés élastiques avec l'élongation est due aux changements de la topographie du reseau.

Quelques observations sont faites sur les changements topologiques des reseaux du vulcanisat à des élongations très élevées. On indique les analogies entre le renforcement par cristallisation forcée et par addition du noir de carbon. Les effets des noirs sont attribués principalement à l'adsorption préférentielle sur les particules des carbones de chaines courtes du reseau, qui deviennent surcontraint aux déformations élevées. Lors de l'adsorption l'énergie cinétique de des chaînes particulières sera dissipée sous forme de chaleur d'adsorption.

On donne des exemples sur l'application de la relation de F. Bueche entre l'extension d'un échantillon et l'extension de la matrice d'un élastomère dans un vulcanisat chargé. Cette equation diffère de celle basée sur la relation d'Einstein pour la viscosité des suspensions qui s'applique à d'autres caoutchoucs chargés. La différence entre ces deux relations peut être associée avec l'absence ou la présence de liaison chimique entre l'élastomère et la charge.

La topographie du reseau exerce une influence sur les proprietés ultimes des vulcanisats. Les échantillons de polybutadiène dans lesquels les réticules sont des simples liaisons, se brisent à des élongations plus basses, que ceux dont les réticules contiennent des chaînes de 18 atoms, à concentrations égales.