NETWORK STRUCTURE AND THE ELASTIC PROPERTIES OF VULCANIZED RUBBER[1]

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CONTENTS

I. INTRODUCTION

As early as 1859 Joule recognized on the basis of his experiments that the retractive force in stretched rubber originates from thermal motions as apart from intermolecular attractive forces. In the language of thermodynamics, the Gough–Joule effect (increase of tension in stretched rubber with temperature, or the thermodynamically related temperature rise during adiabatic stretching) demonstrates that the extension of rubber is accompanied by a decrease in entropy. More recent experimental measurements on the thermoelastic properties of rubber (1, 15, 28, 31) have shown explicitly that this increase in entropy is largely responsible for the retractive force, the change in internal energy with elongation being of minor importance. The problem of rubber elasticity is chiefly concerned, therefore, with an account of the origins of this entropy change accompanying deformation.

Meyer, von Susich, and Valkó (27) in 1932 suggested that the decrease of entropy with elongation is a consequence of orientation of the molecular chains of which rubber is composed. Macroscopic elongation of the specimen requires

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microscopic elongation of the irregular chains which comprise its structure, and an elongated chain represents a less probable (lower entropy) state than an irregular chain of random configuration. Thus, the retractive force is due chiefly to the tendency for the rubber structure to assume a more probable (disoriented) state, and does not arise from attractive forces of one sort or another within the structure.

At the present time the explanation of Meyer, von Susich, and Valkó for the change in entropy of rubber on stretching, and hence for the origin of the major component of the elastic retractive force, is almost universally accepted. The next problem, that of interrelating quantitatively the stress on the one hand with the strain and the network structure on the other, has been attacked by the methods of statistical mechanics. This involves evaluation of the available number of configurations (configurational "probability") as a function of deformation. The relative number of configurations can be converted to an entropy change by employing the Boltzmann relationship, and the stress can be computed from the resulting entropy function by straightforward methods of thermodynamics.

In this paper the various methods which have been advanced for treating the statistics of network deformation will be compared with one another and with experimental results. As an extension of these treatments of rubber elasticity, the effects of network imperfections, such as arise from the finite molecular weight of the unvulcanized rubber, will be incorporated into the theory. The connection between swelling of rubber vulcanizates in solvents and their elastic properties will be discussed.

II. NETWORK STRUCTURE OF VULCANIZED RUBBER

Before proceeding with a discussion of the various methods for dealing quantitatively with the statistics of rubber network deformations, it is necessary to consider briefly the structure of vulcanized rubber. Raw (unvulcanized) rubber consists of very long polymeric molecules, each composed of a thousand or more of the structural unit C_5H_8. In the unoriented (undeformed) state these thread-like molecules are randomly entangled in a completely haphazard manner. The configuration of any individual molecule resembles the path which would be traced by a molecule of a gas in travelling a distance equal to the length of the molecule, the mean free path of the gas molecule being equal to the length of one freely orienting segment of the polymer chain. From the point of view of structure, vulcanization consists of the introduction of intermolecular cross-linkages at randomly selected points of contact between molecules. These cross-linkages may occur on an average of once for every two hundred or so structural units in a soft gum vulcanizate. Thus, each molecule will be cross-linked to other molecules at an average of five or more points, and a continuous network structure will be developed. This network will extend throughout the piece of rubber. It will include very nearly all of the initial rubber molecules, inasmuch as the total number of cross-linkages considerably exceeds the total number of primary molecules[2]. This is a consequence of statistical laws applied to random cross-linking processes (3, 4).

During the cross-linking process the rubber molecules lose their identities as individual units, being replaced by the continuous network structure mentioned above. The primary element of the network is the portion of a rubber molecule extending from one cross-linkage to the next one encountered along the molecule. This structural element will be referred to throughout this paper as a "chain."

Figure 1 represents an attempt to diagram a portion of the network structure, of necessity greatly oversimplified. The actual chains between cross-linkages will be much more irregular and will on the average meander through a considerably larger region of space extending beyond the junction points. Furthermore, other chains and cross-linkages, not immediately connected with those shown in the figure, will interpenetrate this same region of space.

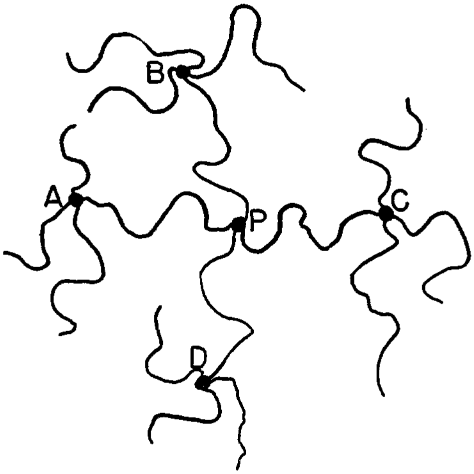

FIG. 1. Diagrammatic representation of a portion of the network structure surrounding the cross-linkage P.

The configurations of the chains in the undeformed piece of rubber will conform to the same description as has been applied to the unvulcanized molecule of raw rubber. Prior to cross-linking each chain exists as an element of a molecule, bound at either end to other similar elements. While its attachments to its neighbors hinder its *rate* of transformation from one configuration to another, they do not influence its *average* configurations. The chain configurations are completely random. Cross-linking does not disturb these configurations; it

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[2] James and Guth (19) estimate that the proportion of vulcanized rubber which is actively combined with the network is small—about 25 per cent of the total. In addition to the fact that a numerical error occurs in their equations, their procedure is based on a hypothetical model for vulcanized rubber which bears little resemblance to the actual structure.

merely tends to fix them. Consequently, the configurations of the chains in undeformed vulcanized rubber are the same as would be assumed by a set of totally independent molecules of the same lengths as the chains.

The cross-linkages represent fixed points in the network structure in the sense that at each of them four chains are permanently connected. A cross-linkage may "diffuse" over a limited region of the space through rearrangements in the configurations of the associated chains. The restraint imposed by a cross-linkage requires that these rearrangements of the associated chains occur in unison in order that the chain ends shall always meet a common point.

Mean positions in space may be assigned to each cross-linkage. When the network is deformed these mean positions will be shifted like minute inclusions in a homogeneous isotropic medium. Thus, an elongation in the z direction with an increase in the length by the factor α will increase the z coördinate of the mean position of junction A with respect to that of P by the factor α. Coördinates in the perpendicular directions, the volume remaining constant, will be decreased by the factor $1/\sqrt{\alpha}$. The deformation produces a change in the distribution of chain "displacement lengths," or distances between chain ends. The result is an increase in the average chain displacement length. Consequently, there is a decrease in the number of configurations available to the system of interconnected chains—in other words, a decrease in the configuration probability. Various methods for arriving at a quantitative estimate of this entropy change will be discussed in the next section.

III. QUANTITATIVE TREATMENT OF RUBBER ELASTICITY

1. The chain length probability distribution

The common basis for all of the various statistical-mechanical derivations of stress–strain relationships for rubber and rubber-like substances is the equation expressing the probability distribution of chain displacement lengths for chains of random configuration. Taking one end of the chain as origin of coördinates, the probability that the other end lies within a volume element located at x, y, z, is expressed as (13, 23):

$$W(x, y, z)\, dxdydz = (\beta^3/\pi^{3/2}) \exp\left[-\beta^2(x^2 + y^2 + z^2)\right] dxdydz \qquad (1)$$

where the parameter β depends on the length of the chain and its flexibility. The nature of this dependence of β on chain structure is of no consequence in the development of elasticity theory; only the form of equation 1 is important. According to equation 1 the root mean square value of the chain displacement length $r(= \sqrt{x^2 + y^2 + z^2})$ must equal $\sqrt{3/2\beta^2}$.

No rigorous proof of the validity of equation 1 as applied to polymer molecules which derive their flexibility from permissible rotations about valence bonds of the chain has been given. However, for the case of "idealized" chains composed of many units joined by bonds at fixed angles about which there is free rotation, each unit possessing length but an inappreciable cross section ("volumeless" chains), the equation seems to be reasonably well founded (13, 23).

Lord Rayleigh's (32) analyses of an analogous problem, that of random flight in three dimensions, provides further support. Kuhn (6, 25) has shown that limitations on free rotation about bonds may be expected to alter β (for chains of given contour length) but not the form of equation 1.

Neglect of the volume occupied by the chain introduces a more dubious approximation. In effect, this approximation fails to exclude from consideration those configurations in which two (or more) units, separated some distance along the chain, would occupy the same element of volume. No quantitative treatment of the effect of this approximation has been carried out. It may be presumed, however, that proper exclusion of these impossible configurations would alter somewhat the character of the distribution.

Mention should also be made of the necessary deviation from equation 1 for large values of r, i.e., for r values approaching that for the fully extended chain. The actual distribution should halt at this limit, instead of approaching zero asymptotically as prescribed by equation 1. James and Guth (19, 20) have discussed this limitation at length, with the conclusion that at elongations above 300 per cent of the initial length the chains in representative vulcanizates are sufficiently extended to justify consideration of this correction. This is about the point at which crystallization sets in in natural rubber. Synthetic rubber pure gum vulcanizates either undergo crystallization at this or slightly higher elongations, or, lacking the ability to withstand the stress which develops, they are ruptured at about this point. Since the statistical treatment of elasticity becomes inapplicable quantitatively when crystallization occurs, it is doubtful that this correction is of any great practical importance.

In this paper we shall employ equation 1 as a reasonable approximation to the correct chain-length distribution function, realizing that it is neither rigorously proved nor quantitatively exact. To the extent that it expresses accurately the probability that a free molecule or chain will possess a displacement length r, it must also represent the relative number of configurations available to the chain for a fixed displacement length r, since the probability of a given state is proportional to the number of configurations consistent with that state. The function W will be referred to interchangeably as an expression for the probability of a given r value and for the relative number of configurations of a chain having the displacement length r.

2. The elastic characteristics of a single chain

We consider a single chain, one end of which is constrained to lie in a volume element about the point located at x, y, z with respect to the other end. Thus, the chain displacement length is fixed, but intervening portions of the chain are free to assume any configuration consistent with bond angles, steric interferences, etc. The configurational entropy of the single chain is given by the log of the number of configurations multiplied by Boltzmann's constant k. Hence, employing equation 1 for the relative number of configurations, there is obtained for the configurational entropy of a single chain, omitting an additive constant

$$s = k \ln W = k[A - \beta^2(x^2 + y^2 + z^2)] \qquad (2)$$

where A is a constant.[3] The maximum entropy occurs when

$$r = \sqrt{x^2 + y^2 + z^2} = 0$$

The force of retraction arising from the entropy change is

$$-T(\partial s/\partial r) = 2kT\beta^2 r \tag{3}$$

i.e., the chain is a Hooke's law spring, the tension in which is directly proportional to its length.

On the basis of this result James and Guth (14, 19, 20) replace the actual network of interconnected chains with a hypothetical "network" composed of three sets of parallel springs running the full length, breadth, and thickness of the piece of rubber. This hypothetical set of springs, it is shown, should reproduce the elastic properties of rubber. After taking into account the effects of an "internal pressure" on elastic properties at fixed volume, the following expression is obtained for the retractive force as a function of the degree of extension α:

$$f = 2mkT\beta^2[\alpha - 1/\alpha^2] \tag{4}$$

The number of parallel chains per unit cross-sectional area of James and Guth's system of springs is represented by m.[4] The dependence of f on α is precisely that found by other methods which treat the statistical mechanics of the actual rubber network. However, the coefficient m, expressing the number of chains *per unit area* of the hypothetical "parallel chain" model, is a fiction in terms of the actual network of irregular chains. The real chains occupy *volume*, not an area. Furthermore, equation 4 is dimensionally incorrect, f being expressed in force per unit volume. (β has the dimensions of reciprocal length.)

In conclusion, this procedure yields a satisfactory form for the dependence of stress on strain (α), but it fails to connect elastic properties with network structure.[5] Thus, the important relationship obtained by other methods (*cf. seq.*) between the elastic force of retraction and the number of chains per unit volume, or the directly related concentration of cross-linkages, is obliterated by the replacement of the network by sets of parallel chains.

3. *Statistical mechanics of the network as a whole*

A simpler and more satisfactory analysis of the elasticity problem can be carried out by considering the statistical mechanics of the network as a whole,

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[3] It may be objected that application of the methods of statistical mechanics, and of thermodynamics as well, to a system composed of only 10^2 to 10^3 units is unsound. While in the above we deal with a single chain, the actual results are to be applied to a system of many chains—some 10^{18} per cubic centimeter. Hence, we are concerned only with the ***average*** characteristics of a single chain.

[4] Substituting $\beta^2 = 3/2\, \bar{r}^2$ in equation 4 yields an expression differing from James and Guth's equation 3.3 of reference 19 by a factor of three, omitted from their equation (their L replaces our r). In an earlier publication (14) the coefficient is correctly expressed as in equation 4 above.

[5] This is in agreement with a conclusion drawn by James and Guth in a comparison of their method with others. See page 377 of reference 19.

without regard for the so-called elasticity of a single chain. This is the method applied by Kuhn (24), Wall (37), and Treloar (35).

The internal state of the network system can be specified in terms of the positions of the cross-linkages. As pointed out earlier, deformation of the rubber transforms the arrangement of these points, and hence alters the internal state of the network. Any such state can be represented by the system of vectors connecting neighboring junction points, i.e., the system of vectors each of which connects the two ends of a chain. If these displacement vectors are shifted to a common origin and the surrounding space is marked off into volume elements numbered 1, 2, 3, etc., the number of vectors terminating in the i^{th} volume element can be designated by ν_i. The state of the system is defined by assigning a value to each of the ν_i, subject, of course, to the condition that $\Sigma\nu_i = \nu$, where ν is the total number of chains. Each chain may assume a number of configurations through rearrangement of intervening portions of the chain, its displacement vector remaining fixed. For chains having vectors terminating in the i^{th} cell, the relative number W_i of these configurations is given by equation 1 with x, y, z corresponding to the coördinates of the i^{th} cell.

The probability P of a given state is given by the product of the probabilities, or relative number of configurations, for each chain. Hence,

$$P = \prod_i (W_i)^{\nu_i} \tag{5}$$

This expression has been employed by Kuhn (24) and Treloar (35).[6] Wall (37) considers that the chains are interchangeable, and includes, therefore, a factor for the number of combinations of a total of ν vectors such that ν_1 of them terminate in cell "1," ν_2 in cell "2," etc. Instead of equation 5, Wall uses the equation

$$P = [\prod W_i^{\nu_i}][\nu!/\prod \nu_i!] \tag{5'}$$

The assumed interchangeability of chains is inconsistent with the mutual interdependence of the chains of the network. However, the second factor in brackets in equation 5′ is of no consequence in deformations unaccompanied by a change in volume. In all such cases this factor remains unchanged, and therefore does not affect the final results.

Taking the logarithm of equation 5 and multiplying by the Boltzmann constant to obtain the entropy:

$$S = k \sum_i \nu_i \ln W_i = k \sum_i \nu_i[A - \beta^2(x_i^2 + y_i^2 + z_i^2)] \tag{6}$$

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[6] Kuhn (24) failed to recognize that the restraints imposed on a chain are limited to its ends, the intervening portions being free to assume whatever configuration is consistent with the given chain displacement length. In his analysis he introduced additional restraints on the mid portion of the chain. Treloar (35) has corrected this error in Kuhn's treatment and has presented an exact solution of the resulting equations instead of the approximate solution limited to very low elongations submitted by Kuhn.

In the undeformed state the distribution of chain displacement lengths will be that given by equation 1, the cross-linkages having been introduced at random between unoriented chains. Then

$$\nu_i = \nu W_i \, dx dy dz$$

If the sample is elongated in the z direction, the length being increased by the factor α, then, under the assumption that the relative positions of the network junctions change in accordance with the macroscopic dimensions of the sample, the z coördinate of each vector will be increased by the factor α and x and y will be decreased by $1/\alpha^{1/2}$, the volume remaining constant. A chain for which the projected distance between its ends is equal to z possessed a component equal to z/α before stretching. Hence to obtain the new distribution of chain lengths after stretching, z in equation 1 must be replaced by z/α. Similarly, x and y must be replaced by $x\alpha^{1/2}$ and $y\alpha^{1/2}$. In place of equation 1 we have, therefore,

$$W'(x, y, z) \, dx dy dz = (\beta^3/\pi^{3/2}) \exp\left[-\beta^2(\alpha x^2 + \alpha y^2 + z^2/\alpha^2)\right] dx dy dz \qquad (1')$$

Substituting $\nu_i = \nu W'_i \, dx dy dz$ in equation 6 and replacing the summation by integrals:

$$S = k\nu(\beta^3/\pi^{3/2}) \iiint_{-\infty}^{+\infty} \exp\left[-\beta^2(\alpha x^2 + \alpha y^2 + z^2/\alpha^2)\right]\left[A - \beta^2(x^2 + y^2 + z^2)\right] dx dy dz$$

Treloar (35) has integrated this expression, obtaining a result which becomes, when expressed as the entropy change in passing from the undeformed state $\alpha = 1$ to the deformed state defined by α:

$$\Delta S = S(\alpha) - S(1) = -k\nu(\alpha^2 + 2/\alpha - 3)/2 \qquad (7)$$

This expression was obtained previously by Wall (37), employing equation 5′ and a different mathematical procedure.[7] The entropy contribution to the elastic retractive force may be computed at once from Wall's equation (equation 7)

$$f = -T(\partial S/\partial L) = -T(\partial S/\partial \alpha)/L_0 = (kT\nu/L_0)(\alpha - 1/\alpha^2) \qquad (8)$$

where L_0 is the initial length of the unstretched sample. This equation, relating the elastic retractive force to network structure as represented by ν and to the deformation α, was first obtained by Wall. The tension τ (force per unit initial cross-sectional area) is given by either of the alternate expressions

$$\tau = RT(\nu/V)\varphi(\alpha) \qquad (9)$$

or

$$\tau = (RT\rho/M_c)\varphi(\alpha) \qquad (9')$$

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[7] In deriving equation 7 all chains have been assumed to be of the same size, i.e., the same contour length. Considering the random nature of vulcanization this obviously is far from fact. For a system of heterogeneous chains, this same procedure may be applied to each set of chains of a given size. The final result summed over all sizes of chains is precisely equation 7, where ν is the total number of chains of all sizes.

where ν is the number of chains in the volume V, M_c is the molecular weight per chain (number average), ρ is the density of the rubber, and

$$\varphi(\alpha) = \alpha - 1/\alpha^2 \tag{10}$$

Whereas the previous equation (4) contains the $\varphi(\alpha)$ function, the dependence of the coefficient on the number of chains, or on the concentration of cross-linkages, does not occur therein. The simple connection between the elastic "modulus" and network structure provided by equations 8, 9, or 9′ is of the utmost importance.

4. The tetrahedral model for the network structure of rubber

An alternative procedure (7) for statistical treatment of rubber network deformations can be carried out in terms of an average "cell" of the network.[8] Instead of considering the chains as individual elements, the four chains meeting at a junction are considered mutually. The four chains radiating from each junction lead to four "nearest neighbor" junctions, the average positions of which define a tetrahedron. One such tetrahedron is defined by the points A, B, C, and D in figure 1, considered in three dimensions. If we idealize the network to the extent of making all chains of the same size (same contour length), then the *average* tetrahedron, or "cell," so defined will be a *regular* tetrahedron. It should be made clear at the outset that, owing to the intertwining of the chains, these tetrahedral cells will overlap extensively, a given element of the volume being encompassed by many of these elementary tetrahedra. These cells do not adjoin one another with the regularity and volume-filling character of the unit cells of a diamond lattice, for example.

The tetrahedral cell is represented diagrammatically in figure 2. The existence of this cell as a unit of the network structure rests entirely upon the requirement that four chains extending from the corners (A, B, C, and D) shall meet within a volume element $\Delta\tau$ at some point P. The relative number of configurations available to the system of four chains which meet within a *particular* volume element $\Delta\tau$ is given by the product of four "probabilities" for the individual chains

$$P(\Delta\tau)^4 = \prod_{i=1}^{4} [W(x_i y_i z_i)\Delta\tau_i]$$

where x_i, y_i, z_i, etc. are the coördinates of the same volume element $\Delta\tau$ referred, respectively, to the four corners of the tetrahedron A, B, C, and D. Substituting from equation 1 and integrating over the space in order to obtain the relative number of configurations when the chains meet in the same volume element located *any place:*

$$P(\Delta\tau)^3 = (\beta^{12}/\pi^6)\left[\int_\tau \exp\left(-\beta^2 \sum_{i=1}^{4} r_i^2\right)\Delta\tau\right](\Delta\tau)^3 \tag{11}$$

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[8] The derivation given here is a simplification of the more rigorous treatment by Flory and Rehner (6, 7).

It can be shown from the geometry of the tetrahedron that

$$\sum_{i=1}^{4} r_i^2 = 4a^2 + 4\lambda^2(\alpha^2 + 2/\alpha)/3$$

where a is the radial distance of P from the center O of the tetrahedron, λ is the distance from O to one of the corners of the undeformed tetrahedron, and α is the relative elongation of the tetrahedron resulting from deformation of the piece of rubber without change in volume. The average tetrahedron is assumed to be deformed in proportion to the changes in macroscopic dimensions. Substituting in equation 11:

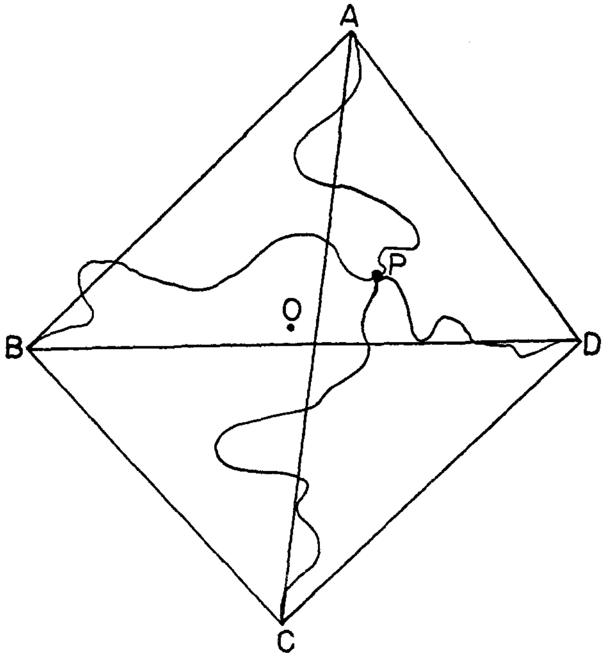


FIG. 2. Unit tetrahedral "cell" surrounding the central junction P

$$P = (4\beta^{12}/\pi^5)\int_0^\infty \exp\,[-4\beta^2 a^2 - 4\beta^2\lambda^2(\alpha^2 + 2/\alpha)/3]a^2\,da \qquad (12)$$

The relative configurational probability for the stretched and normal states is obtained by dividing $P(\alpha)$ by $P(1)$. Dividing equation 12 by its value for $\alpha = 1$, the relative configurational probability of the stretched rubber becomes

$$P(\alpha)/P(1) = \exp\,[-4\beta^2\lambda^2(\alpha^2 + 2/\alpha - 3)/3] \qquad (13)$$

The distance λ from the center to a corner of the undeformed tetrahedron may be taken equal to the root mean square chain displacement length (r) which, according to equation 1, is equal to $\sqrt{3/2\beta^2}$. Then, taking the logarithm of equation 13 and multiplying by Boltzmann's constant, the entropy of deformation becomes

$$\Delta s = -2k(\alpha^2 + 2/\alpha - 3)$$

for the tetrahedral cell. Since each cell contains four chains, multiplication by $\nu/4$ should give the entropy change for the network as a whole. The result is identical with Wall's equation (equation 7), from which the elasticity equations (8 and 9) are derived by standard procedures of thermodynamics.

IV. COMPARISON OF THE THEORY WITH EXPERIMENTAL RESULTS

In the preceding section it has been shown that the various statistical-mechanical treatments of rubber elasticity agree on the form of the force–elongation relationship for vulcanized rubber as represented by equation 10. Isothermal stress–strain curves for rubber (1, 16, 26, 36), synthetic rubber (31), and rubber-like polymers (29) are reasonably well reproduced by this function at elongations preceding the onset of crystallization. The experimentally determined contribution to the retractive force of the change in heat content on stretching is very small compared with the total tension. This term, which has been neglected in the above theory, does not alter the force–elongation curve significantly below the region of crystallization (1, 36). Treloar has shown that measurements on natural rubber in compression ($\alpha < 1$) are in excellent agreement with equation 10.

It is significant that the form of the dependence on α (i.e., $\varphi(\alpha)$) is unaffected by the degree of cross-linking. Stress–strain curves for different degrees of vulcanization, therefore, should be superimposable by altering the stress scale by suitable factors. This prediction finds verification for natural rubber (16) and Butyl rubber (10) vulcanizates differing in degree of cure. Hence a single quantity, the stress at a given elongation, will suffice to characterize the stress–strain curve as a function of the degree of vulcanization, except at higher elongations where crystallization sets in.

The connection between elastic properties and vulcanizate structure is of more far-reaching importance than the exact form of the stress–strain curve. Wall's equation (9), which is substantiated by Treloar's modification of Kuhn's treatment and by the method of Flory and Rehner, furnishes an explicit expression for the constant of proportionality between $\varphi(\alpha)$ and the absolute tension. This proportionality constant contains the number of chains, ν, which for an ideal network formed from indefinitely long primary molecules must equal twice the number of cross-linkages. Thus, the tension at any given elongation is predicted to be proportional to the degree of cross-linking of the molecules.

The degree of cross-linking in a vulcanizate is not easily determined directly. Prior to a recent investigation (10) of the physical properties and structure of Butyl rubber, no comparison between the tension at a given elongation and the independently estimated degree of cross-linking in a vulcanized rubber were available. Butyl rubber, a copolymer of isobutylene with a small percentage of a diolefin, provides an ideal case for such a test, inasmuch as the cross-linking capacity can be controlled through the diolefin content of the polymer. The concentration of cross-linkages formed in the vulcanization (fixed recipe) of Butyl polymers of a given diolefin content was determined as follows: Raw polymers were separated by fractionation into a series of samples of comparatively narrow molecular weight range, each of which possessed the same percentage of unsaturated (diolefin) units and, hence, the same cross-linking capacity. Each of these was compounded and cured under standardized conditions; thus were produced in each sample the same number of cross-linkages per unit amount of polymer. The vulcanizates were extracted with cyclohexane at room temperature to remove soluble constituents. These are negligible for fractions of

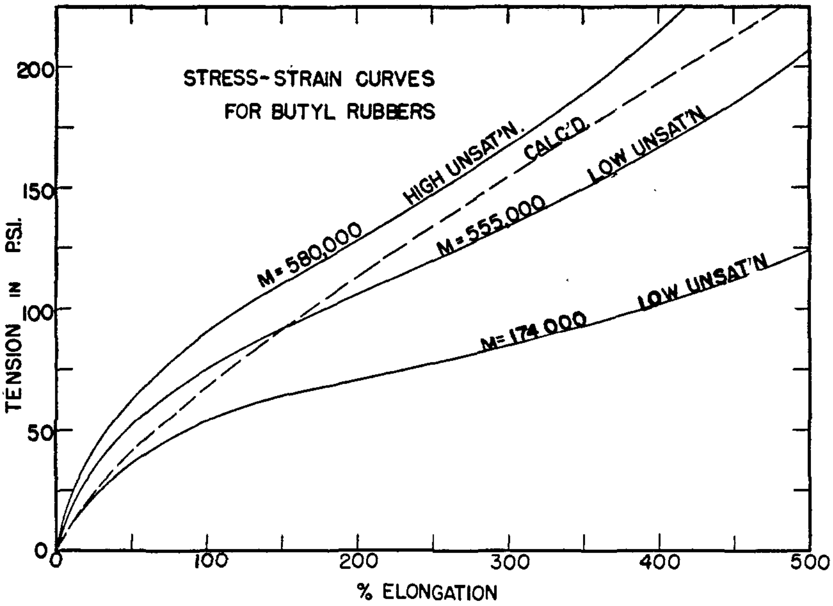


FIG. 3. Stress-strain curves for several pure gum vulcanizates from fractionated Butyl rubber polymers. Molecular weights are indicated. The calculated curve represents $\varphi(\alpha)$ as given by equation 10.

high molecular weight, where each molecule on the average enters into a number of cross-linkages. As the molecular weight is decreased the percentage of "sol" eventually increases rapidly, reaching 100 per cent at the "gel point" or critical molecular weight M' for incipient insolubility. This critical molecular weight was estimated by an extrapolation of the percentage of sol plotted against molecular weight of the fraction.

From the theory of random cross-linking (3, 4, 34) it is known that for molecules of uniform length incipient gelation occurs when the number of cross-linkages equals half the number of initial molecules. Hence, the concentration of cross-linkages in moles per gram is equal to $1/2M'$ throughout the entire series of vulcanizates from polymers of the same cross-linking capacity. Recalling that in a network formed from indefinitely long molecules the number of chains is twice the number of cross-linkages, it is evident that M_c equals M', the critical molecular weight for incipient gelation at fixed cross-linking capacity.

Several stress–strain curves for Butyl rubber vulcanizates prepared from fractionated samples differing in molecular weight and in unsaturation are shown in figure 3. The values for M_c, estimated as outlined above, are 35,000 and 20,000, respectively, for the vulcanizates from the low and high unsaturation samples. The tensions at 300 per cent elongation for the high-molecular-weight rubbers, 108 and 134 pounds per square inch, respectively, are greater than the values, 38 and 66 pounds per square inch, calculated from the M_c's using equation 9′. In addition to the discrepancy in magnitudes, the change in "modulus" with the degree of cross-linking is less than a direct proportionality predicted by theory. Furthermore, the dependence on molecular weight is rather large.

Correlation between the above theory and experimental results on the stress–strain properties of rubber and rubber-like materials may be summarized as follows: The statistical theory of rubber elasticity predicts a form for the stress–strain curve which is in good agreement with experiment. The effect of change in heat content with elongation is small. On the other hand, the magnitude of the observed tension at a given elongation is somewhat larger than the above theory predicts, at least in the case of Butyl rubber. The tension varies less rapidly with the concentration of cross-linkages than the predicted direct proportionality. The large observed dependence on the initial molecular weight of the unvulcanized polymer is nowhere taken into account in the above theory. Further refinements of the theory discussed in the next section provide explanations for these deviations.

V. NETWORK DEFECTS: THE INFLUENCE OF MOLECULAR WEIGHT ON ELASTIC PROPERTIES

The various derivations of the basic equations 9 and 9′ stem from the same physical concepts of network structure. In attempting refinements which will remove the discrepancies between theory and experiment pointed out above, it will be necessary therefore to reconsider this structure in greater detail.

1. Network entanglements

The fact that the elastic force of retraction in Butyl rubber vulcanizates exceeds the value calculated from equation 9, in which $\nu/2$ is identified as the number of chemical cross-linkages, suggests that types of chain interactions other than primary valence attachments between chains are to be reckoned with. Several possibilities require consideration.

Attachments between chains due to van der Waals forces have been postulated as a source of cross-linkages in rubber-like materials. There is no doubt as to the existence of such forces between polymer molecules. The question of concern here is the permanence with which these forces may unite neighboring chains. In order for such an attachment to function as a network cross-linkage, obviously it must endure at least over the interval of the elasticity measurement. On the other hand, the existence of the rubbery state in any high polymer predicates a high degree of internal mobility which will allow elements of the chains to slip past one another during deformation. van der Waals attractions between chains must be small in order for the material to be rubber-like.

In harmony with this deduction rubber-like materials usually possess non-polar (hydrocarbon) chains or, if they contain strong polar groups, rubber-like character is exhibited only at elevated temperatures or in the presence of a solvent or plasticizing substance capable of satisfying the forces of the polar groups. The probable existence of occasional strong polar, or possibly ionic, interchain bonds in certain rubbery materials cannot be denied, e.g., in aqueous protein gels and possibly to a very limited extent in raw, unmasticated natural rubber containing traces of polar substituents (30). The occurrence of a significant number of such bonds in vulcanized natural rubber or in hydrocarbon synthetic rubbers is exceedingly unlikely in view of their non-polar nature and the consequent weak van der Waals forces between chains. If such bonds contributed to the elastic properties, their number should decrease with temperature and the elastic retractive force should show a corresponding diminution, which is contrary to observation. Furthermore, the correlation of swelling behavior of Butyl vulcanizates with elastic properties (*cf. seq.*) demonstrates that about as many cross-linkages are operative in the presence of solvent as in its absence. van der Waals bonds would be expected to be eliminated, or at least diminished in number, in the presence of a solvent.

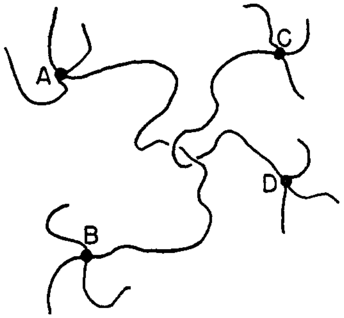


FIG. 4. Entanglement of chains within the network structure

It has been suggested (12) that long chains, merely owing to their irregular configurations, become entangled with one another to the extent that a molecule is unable to extricate itself from its neighbors. Two arguments, one theoretical and the other based on direct experiments, can be leveled against the view that these entanglements of linear (non-network) molecules are equivalent in their contribution to elasticity to permanent, or primary valence, cross-linkages. Investigations of electrical (11) and viscous (2, 21) properties of polymers in the rubber-like or liquid state reveal that within each chain small elements, or segments, composed of perhaps ten or twenty chain atoms are constantly rearranging their positions at a rapid rate under the influence of thermal agitation. Successive random rearrangements of these segments lead to diffusion not only of the segments but of the molecule as a whole from one configuration and position to another. Hence, a molecule does not maintain fixed relationships with respect to its neighbors. Although entanglement of linear molecules is a factor contributing to resistance to flow (high viscosity) and to a low *rate* of solution, it should not be expected to eliminate plastic flow or to affect *equilibrium* solubility. These contentions are confirmed by experimental results: All linear polymers regardless of molecular weight display the properties of unvulcanized rubber above their brittle point temperatures, i.e., they are soluble in suitable solvents and under stress they undergo plastic flow at a non-diminishing rate.

The situation is otherwise if there exists a primary valence network structure. Here entanglements of chains may lead to restraints which are equivalent to additional chemical cross bonds in their contribution to network properties. Consider, for example, two chains, one looped about the other, such as are shown in figure 4. While the chains AB and CD are not bound together at fixed points as in a chemical cross-linkage, they nevertheless are permanently prevented from crossing each other. The configurations available to each chain are limited by interference with the other. This type of restraint, which will be called a network entanglement, is of a permanent nature; it cannot be circumvented without disrupting a portion of the primary valence network. One of these entanglements may not be quantitatively equivalent to a chemical cross bond in its contribution to elastic properties. However, a number of them along each chain may raise the effective number of cross-linkages appreciably above the actual number.

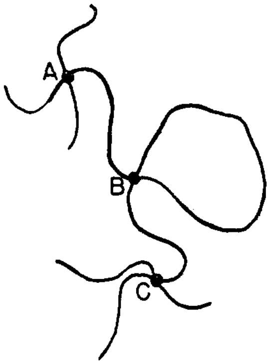


FIG. 5. Intramolecular cross-linking

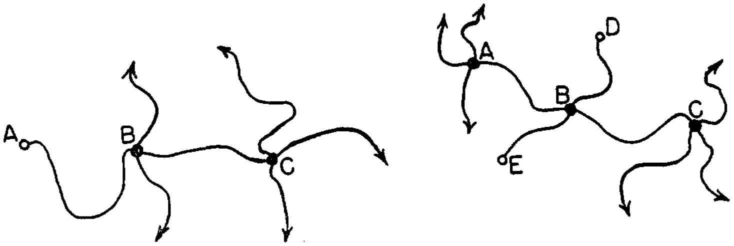
It should be reëmphasized that these network entanglements would offer no permanent barriers to chain configuration were it not for the chemical cross bonds which are responsible for the primary valence network structure. Their existence as permanent features of the structure is dependent upon the presence of primary valence cross-linkages.

2. *Intramolecular cross-linkages*

Occasionally two parts of the same molecule may become cross-linked, thus forming a loop as shown in figure 5. If there are no other intervening cross-linkages with other chains along the loop, then configurations of the loop will be unaffected by deformations. This portion of the structure can contribute no reaction to deformation. The entire portion between the cross-linkages A and C will act as a single chain, and the cross-linkage B is wasted. Cross-linkages of this type should be deducted from the total number in obtaining the number of effective cross-linkages. Estimates of the number of such intramolecular cross-linkages for flexible chains of random configuration indicate that they constitute only a few per cent of the total. Their further consideration is scarcely warranted at the present time.

3. Terminal chains: the effect of initial molecular weight

Previous treatments (7, 14, 19, 20, 35, 37) of rubber elasticity have disregarded the influence on network structure and properties of the molecular weight of the initial rubber molecules from which the network is formed by vulcanization. In other words, the molecules were assumed to be infinitely long. Experiments already have been quoted which emphasize the marked dependence of elastic properties on initial molecular weight of the raw rubber. These are supported by widespread experience in rubber technology. The reason for this dependence is found in the fact that each end of an initial molecule contributes a flaw to the final network structure. The portion of a molecule from one end to its first cross-linkage along its length, as depicted in figure 6a, contributes nothing to the response of the network to deformation. The chain AB is always free to assume any configuration whatever, owing to the freedom of the end A. Similarly, attachment of the network at the point B in figure 6b, to a molecule such as DE which is bound to the network at no other point produces no increase in the effective number of chains. Not only are the two chains DB and BE of molecule DE inactive, but the cross-linkage at B is not a point of constraint on the chain AC. Hence, the portion of the network from A to C is to be considered as a single chain, as if the cross-linkage at B were not present.



(a) (b)

FIG. 6. The effect of ends of molecules on network structure: ● indicates a cross-linkage, ○ the terminus of a molecule, and → signifies continuation of the network structure.

This discussion of imperfections in networks of finite chains might be extended to more complex situations. However, the above should be sufficient to demonstrate qualitatively the manner in which finite molecule length will affect the network structure. Quantitative derivation of the effect of molecule length on network properties can best be accomplished by assuming a different approach.

We consider the process of network formation by successive cross-linking of molecules. Let it be supposed that cross-linking is allowed to occur only between molecules, or cross-linked combinations of molecules, which have not been connected directly or indirectly by previously introduced cross-linkages. When there are a total of $N - 1$ cross-linkages connecting N primary molecules "intermolecularly,"[9] all molecules will be bound to a single ramified structure. Before allowing the cross-linking process to continue further, let us consider the properties of the macrostructure developed at this stage. It would be incorrect to call it a network, inasmuch as it contains no net-like structure, i.e., it possesses no circuitous connections within its structure. Because of this fact one portion of the structure can be shifted to a new position or configuration without affecting permanently the configurations of other parts. So far as their average configurations (as apart from their positions in space) are concerned, the various elements of the structure are independent of one another. Likewise, macroscopic deformation does not impose permanent restraints on the configurations of component portions of the structure. This somewhat hypothetical structure should be expected to display a static modulus of elasticity equal to zero.

Additional cross-linking necessarily will be "intramolecular." Closed circuits of interconnected molecules will be produced, and the structure can then properly be referred to as a network. It becomes apparent that it is these circuitous paths in the network which are effective in transmitting the effects of changes of configuration of one part of the structure to another part. Macroscopic deformation can no longer occur without a change in internal configuration which cannot be dissipated through chain rearrangements, barring primary valence rupture. A little consideration will show that for each additional network cross-linkage one new closed circuit, and two active network chains, are formed. (It will be recalled that the number of chains in an ideal network formed from "infinitely" long molecules is twice the number of cross-linkages.)

In the course of the actual formation of the network, intermolecular and intramolecular cross-linking are not sharply differentiated. Nevertheless, the number of circuitous paths in the network, exclusive of non-network, or sol constituents, necessarily will be equal at any stage of the process to the total number of cross-linkages, $\nu_0/2$, in the network minus the number, $N - 1$, of cross-linkages required to combine the primary molecules into a single continuous structure without intraconnecting two parts of the structure to form closed circuits. Hence, the total number of circuitous paths in the network, or, alternatively, the total number of "intrastructural" cross-linkages, will be

$$\nu/2 = \nu_0/2 - N$$

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[9] The term "intermolecular" cross-linkages is used in this and the succeeding paragraph to refer to cross links connecting previously separate molecular species. Each of these may be a cross-linked combination of "molecules" in the restricted sense of primary linear rubber molecules, as employed elsewhere in this paper.

wherein $N - 1$ is replaced by N. The effective number of chains will be given by twice this quantity, or

$$\begin{aligned} \nu &= \nu_0(1 - 2N/\nu_0) \\ &= \nu_0(1 - 2M_c/M) \end{aligned} \tag{13}$$

By introducing this expression into equation 9 or 9′, a revised relationship between elastic retractive force and network properties is obtained which takes into account the effects of finite length of the initial molecules. This equation may be written

$$\tau = (RT\nu_0/V)(1 - 2M_c/M)\varphi(\alpha) \tag{14}$$

Before discussing this equation further, two aspects of its application should be clarified. In the first place the manner in which the occurrence of network entanglements such as have been discussed above will require modification of equation 14 must be considered. Inasmuch as entanglements affect only the active chains of the network, and not the terminal inactive chains such as AB in figure 6a, their effect to a first approximation should be proportional to the number ν of active chains and not to ν_0. It will be necessary, therefore, to increase ν in equation 13 by a factor g. This factor probably will depend on M_c and perhaps on the character of the vulcanization (*cf. seq.*). The modified equation for the tension becomes

$$\tau = (RTg\nu_0/V)(1 - 2M_c/M)\varphi(\alpha) \tag{14'}$$

It is important to note that the factor which introduces the correction for the molecular weight M of the primary rubber molecules is unaffected; M_c refers to the average molecular weight between primary valence cross-linkages, unmodified by entanglements.

Secondly, the above method for computing the number of closed circuits in the network requires revision when the average number of cross-linkages attached to each molecule is small. Here an appreciable proportion of the material consists of a sol fraction which is unattached to the network structure. The proportion of sol is determined (3, 4) by the "cross-linking index" γ, which for primary molecules of uniform length is equal to ν_0/N, i.e., to twice the ratio of cross-linkages to primary molecules. Incipient network formation[10] occurs at $\gamma = 1$. As the number of cross-linkages is increased, the proportion of gel (network) increases rapidly toward an asymptotic 100 per cent. It is only the gel fraction which is responsible for elasticity. Hence, in employing equation 13, ν_0 and N should refer exclusively to the gel fraction. Equations have been derived previously (4) for obtaining the cross-linking index, γ'', for the gel and the percentage of gel from the cross-linking index, γ, of the material as a whole. ν_0 and N for the gel alone can then be computed and the revised expression for ν introduced in place of equation 13. Trial calculations of this sort show that above $\gamma \sim 3$, where the percentage of sol is small, no appreciable error results if ν_0 and N are allowed to refer to the total material without distinguishing sol

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[10] For a system of molecules of non-uniform length, Stockmayer (34) has shown that γ should be taken as the *weight average* number of points of cross-linkages per molecule.

from gel. Hence, so long as M is at least three times M_c, the second factor in equations 14 and 14′ requires no correction for the existence of a small fraction of inactive sol.

4. Comparison of revised equations with experimental results

In figure 7 the force of retraction at 300 per cent elongation ($\alpha = 4$) for a series of pure gum Butyl rubbers (10) vulcanized to the same degree of cross-linking (constant M_c) is plotted against the reciprocal of the molecular weight prior to vulcanization. Fractionated polymers of relatively homogeneous molecular weight were used. The plot is observed to be linear, in agreement with equations 14 and 14′, over the range $M = 114{,}000$ to $730{,}000$. The equation of the straight line in pounds per square inch is

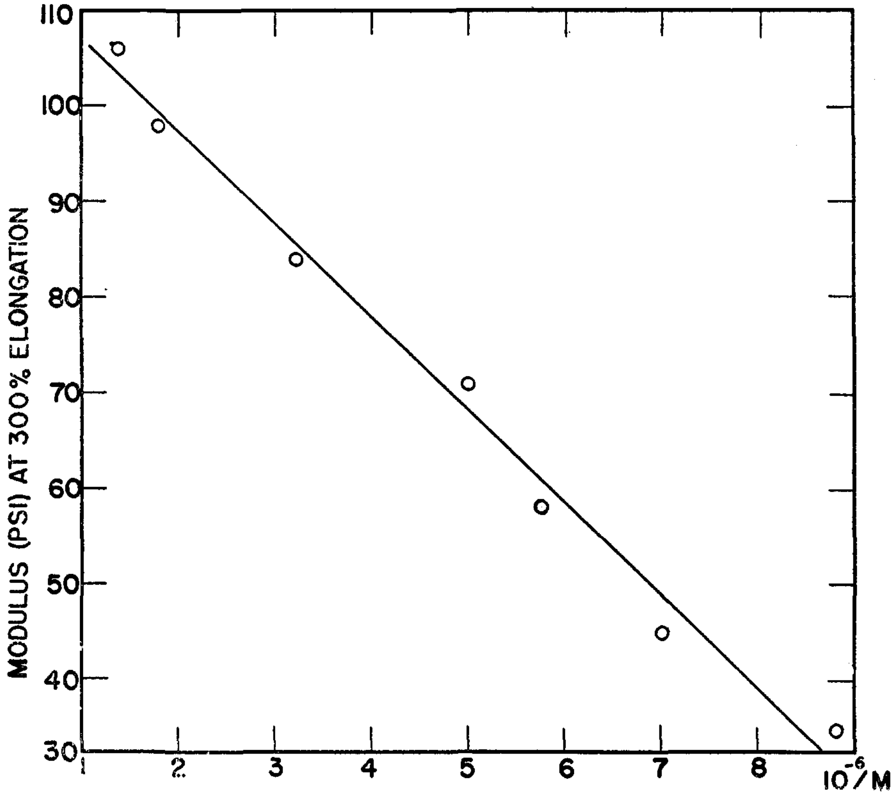

FIG. 7. Relationship between modulus and swelling. Tension ("modulus") at 300 per cent elongation for a series of Butyl vulcanizates having the same concentration of cross-linkages, plotted against the reciprocal of the molecular weight of the polymer before vulcanization.

$$\tau_{300\%} = 127(1 - 77{,}000/M)$$

The indicated value of M_c is 38,500, in good agreement with the figure of 35,000 independently estimated as described earlier in this section. Taking $M_c = 35{,}000$, the value of g in equation 14 calculated from the above coefficient is 3.3.

A similar series for which M_c was estimated to be 20,000 yielded an intercept at about 140 pounds per square inch, corresponding to $g = 2.1$.

The results shown in figure 7 furnish excellent confirmation for the second factor in equations 14 and 14′ and for the explanation which has been given for the influence of molecular weight prior to vulcanization on elastic properties of the vulcanizate. The effects of entanglements in augmenting the elastic tension appear to be rather large. As the degree of cross-linking is increased, and M_c decreases correspondingly, the entanglement coefficient g decreases, presumably owing to the diminished number of entanglements per chain as the average length of the chains is reduced.

These rather large g factors may in part be due to a peculiarity of Butyl vulcanizates. In the vulcanization of this rubber there are only a limited number of points at which cross-linking may occur,—namely, at the diolefin units which are present only in relatively very small number. Furthermore, the process probably is exhaustive; all diolefin units either enter into cross-linkages, or are permanently lost for this purpose owing to side reactions in the sulfur vulcanization process (10). In order for the rarely occurring unsaturated units to meet in juxtaposition, some extreme configurations probably are required. In these the degree of entanglement may be much greater than would occur in a more highly unsaturated rubber in which vulcanization is possible at almost any point where two chains meet.

VI. THE RELATIONSHIP BETWEEN SWELLING CAPACITY OF RUBBER VULCANIZATES AND ELASTIC PROPERTIES

1. Theory

In contrast to plastic raw rubber, vulcanized rubber swells without dissolving when placed in a solvent. This swelling process continues until an equilibrium state is reached, at which the volume of the swollen gel may exceed the initial volume of dry rubber five- to ten-fold (33, 38). Swelling of the rubber involves a distortion of the network structure not unlike that accompanying stretching, except that swelling is isotropic in three dimensions. Swelling equilibrium represents a balance between two opposing tendencies: the ordinary gain in entropy resulting from mixing of the two substances, and the decrease in entropy due to distortion (expansion) of the network. Since the forces associated with the latter change originate from the same source as the elastic retractive force, it is not surprising that elastic properties and swelling capacity are closely related (22, 33).

A detailed analysis of the thermodynamics of swelling has been carried out by Flory and Rehner (6, 8), employing the tetrahedral model for network structure previously discussed. Here a simpler treatment parallelling the Kuhn–Treloar procedure for elastic deformation will be given.

The partial molal free energy of dilution of polymer with solvent has been shown by Huggins (17) and the writer (5) to be given by

$$\Delta \bar{F}_{m,1} = RT[\ln (1 - v_2) + v_2 + \mu v_2^2] \qquad (15)$$

where v_2 is the volume fraction of polymer and μ is a parameter which contains a heat of mixing term (temperature dependent) and an empirical constant the origins of which are not altogether clear (9). For present purposes it will suffice to consider μ as a parameter characteristic of any given liquid pair (18),—solvent and polymer.

The expansion of the network which accompanies absorption of solvent produces a decrease in configurational entropy of the network, an expression for which can be derived by a procedure paralleling the derivation of equation 7 for the change in entropy on stretching. The relative volume increase (ratio of volume of swollen gel to volume of dry rubber) is equal to $1/v_2$. For isotropic swelling, each linear dimension will increase by the factor $1/v_2^{1/3}$. Following the Kuhn–Wall–Treloar procedure, we again assume that the relative positions of the network junctions change in proportion to the macroscopic dimensions. By analogy with equation 1′, the distribution of chain displacement lengths in the swollen "gel" is expressed by

$$W''(r)\,dr = (4\beta^3/\pi^{1/2})\exp(-\beta^2 r^2 v_2^{2/3})v_2 r^2 dr \qquad (1'')$$

where $x^2 + y^2 + z^2$ has been replaced by r^2. Substituting $\nu_i = \nu W_i''\,dr$ in equation 6, the configurational entropy of the swollen network becomes

$$S = (4k\nu\beta^3/\pi^{1/2})\int_0^\infty [\exp(-\beta^2 r^2 v_2^{2/3})][A - \beta^2 r^2]v_2 r^2 dr$$

Integrating and subtracting S for $v_2 = 1$, the network entropy change due to swelling is given by the equation

$$\Delta S_e = -(3k\nu/2)(1/v_2^{2/3} - 1) \qquad (16)$$

Aside from whatever heat of interaction between solvent and polymer may accompany the absorption of solvent (and this has already been included in μ of equation 15), the expansion of the network involves no change in internal energy; it is purely a configurational change. Hence, the free energy of expansion of the network is given by the alternate expressions

$$\begin{aligned}\Delta F_e &= (3kT\nu/2)(1/u_2^{2/3} - 1)\\ &= (3kT\nu/2)\{[Z\nu + n)/Z\nu]^{2/3} - 1\} \qquad (17)\end{aligned}$$

where v_2 has been replaced by its equivalent $Z\nu/(Z\nu + n)$, where n is the number of solvent molecules, ν is the number of chains, and Z is the ratio of the average size (volume) of a chain to the size of a molecule of solvent. Differentiating equation 17 with respect to n, the contribution to the partial molal free energy due to the reaction of the network to swelling is found to be

$$\Delta\bar{F}_{e,1} = (RT/Z)[Z\nu/(Z\nu + n)]^{1/3} = RTv_2^{1/3}/Z$$

Replacing Z by $M_c/\rho V_1$, where V_1 is the molar volume of the solvent and ρ is the density of the undiluted rubber:

$$\Delta\bar{F}_{e,1} = (RT\rho V_1/M_c)v_2^{1/3} \qquad (18)$$

The partial molal free energy change, due both to mixing of the chains with solvent and to expansion of the network, is given by

$$\begin{aligned}\Delta \bar{F}_1 &= \Delta \bar{F}_{m,1} + \Delta \bar{F}_{e,1} \\ &= RT[\ln (1 - v_2) + v_2 + \mu v_2^2 + (\rho V_1/M_c)v_2^{1/3}\end{aligned} \tag{19}$$

Although this equation has other applications (8), we shall be concerned here only with equilibrium swelling, which is so closely related to elastic properties. At equilibrium with excess pure solvent $\Delta \bar{F}_1 = 0$. From equation 19

$$M_c = -\rho V_1 v_2^{1/3}/[\ln (1 - v_2) + v_2 + \mu v_2^2] \tag{20}$$

where v_2 now represents the volume fraction at swelling equilibrium. Hence, given the value of the parameter μ for a given solvent–polymer pair it is possible to calculate the average molecular weight per chain, or the effective concentration of cross-linkages, from the equilibrium swelling volume. For sufficiently large degrees of swelling (small v_2) the quantity in brackets in equation 20 may be approximated by the first term in its series expansion, $v_2^2(1 - 2\mu)/2$, giving

$$M_c \cong 2\rho V_1/v_2^{5/3}(1 - 2\mu) \tag{21}$$

or

$$v_2 \cong [2\rho V_1/M_c(1 - 2\mu)]^{3/5} \tag{22}$$

Hence the swelling volume ratio, $1/v_2$, is proportional to the three-fifths power of the molecular weight per chain.

Substituting equation 20 in equation 9′ to obtain the relationship between tension in stretched rubber and equilibrium swelling

$$\tau = -[RT\varphi(\alpha)/V_1 v_2^{1/3}][\ln (1 - v_2) + v_2 + \mu v_2^2] \tag{23}$$

or

$$\tau \cong RT\varphi(\alpha)(1 - 2\mu)v_2^{5/3}/2V_1 \tag{24}$$

According to this relationship the tension at a given elongation, or "modulus," should be approximately inversely proportional to the five-thirds power of the swelling volume ratio in a given solvent.

2. Comparison with experiment

Experimental results on Butyl rubber pure gum vulcanizates are in good agreement with this relationship. This is shown in figure 8, where the log of the "modulus" at 300 per cent elongation ($\alpha = 4$) is plotted against the log of the swelling volume ratio in cyclohexane at 25°C. The points represent rubbers differing both in initial molecular weight and in degree of cross-linking. The straight line in figure 8, drawn with the theoretical slope of $-5/3$, is matched by the points within experimental error. Taking $V_1 = 110$ cc., the position of this line yields for μ the reasonable value of 0.3 (18) for solutions of Butyl polymers in cyclohexane.

The success of the theory in relating swelling to elastic modulus shows that the same network cross-linkage and entanglements are operative both in swelling and in stretching. If the excess in the modulus over that which would be calculated from the number of primary valence cross-linkages has been correctly attributed to entanglements, these same entanglements produce an equivalent reaction to expansion of the network by a solvent. Similarly, it follows from the above correlation that the effect on equilibrium swelling of molecular weight prior to vulcanization parallels its effect on elastic retractive force as previously discussed. In the equations given above, therefore, the effective number of chains should be employed. For example, in place of equations 17 we have

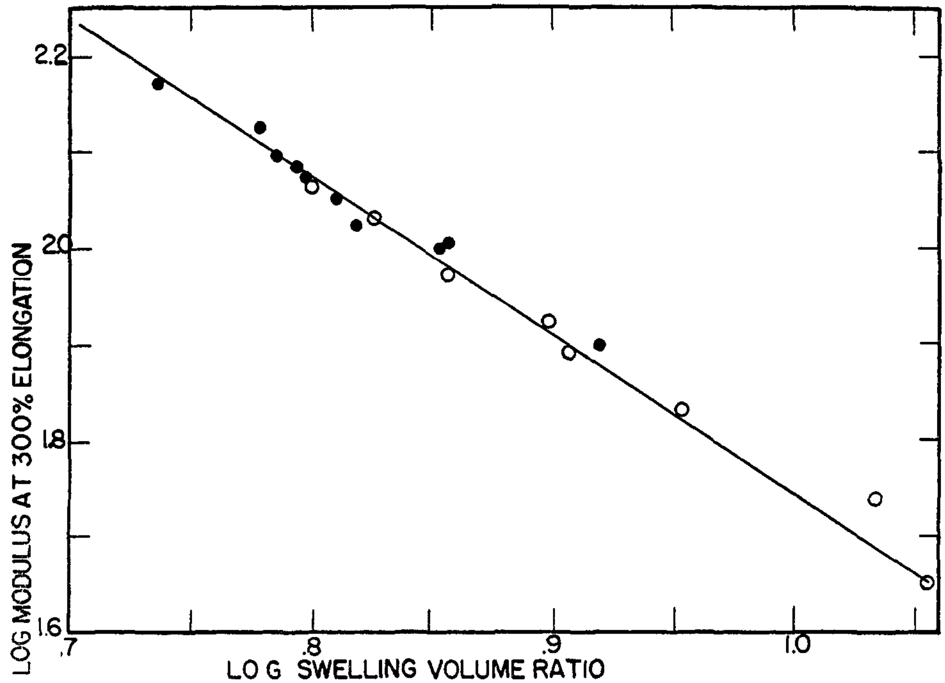

Fig. 8. Relationship between "modulus" and swelling volume ratio ($1/v_2$) for various pure gum Butyl vulcanizates. ○ = low unsaturation series; ● = high unsaturation series.

$$\Delta F_e = (3kTg\nu_0/2)(1 - 2M_c/M)\{[(Z_0\nu_0 + n)/Z_0\nu_0]^{2/3} - 1\} \qquad (17')$$

and in subsequent equations M_c should be replaced by $M_c/g(1 - 2M_c/M)$. The equation for equilibrium swelling becomes

$$v_2 = [2\rho V_1 g(1 - 2M_c/M)/M_c(1 - 2\mu)]^{3/5} \qquad (22')$$

If secondary valence cross-linkages between chains were to contribute to the modulus in deformation, these bonds would be expected to dissociate in the presence of a solvent and the above correlation between swelling equilibrium and modulus would be destroyed. These results constitute strong evidence against the existence of van der Waals cross-linkages in vulcanized rubber.

VII. SUMMARY

Current concepts of the network structure of vulcanized rubber have been reviewed and various recent theoretical treatments of the rubber elasticity problem have been compared. These are found to be in essential agreement; they represent merely different methods of analysis of equivalent physical concepts.

The theoretically derived equation for the elastic retractive force in stretched rubber consists of two factors, one of which is a function of the relative length (α) alone, and the other of which is proportional to the "effective" number of cross-linkages in the network and is independent of the deformation. (The latter factor also contains the absolute temperature.) Experimental results are in agreement with this separability of the elongation and structure factors; i.e., the *shape* of the stress–strain curve (short of the region of crystallization) is preserved as the effective number of cross-linkages in the vulcanizate is varied.

The observed magnitude of the retractive force at a given elongation is appreciably greater than that calculated from the independently estimated number of chemical cross-linkages in vulcanizates of Butyl rubber. This discrepancy is believed to be due to entanglements of the chains which increase the effective number of cross-linkages. The observed effect of the molecular weight of the rubber before vulcanization on elastic properties of the vulcanizate has been taken into account by an extension of previous theories. The "flaws" introduced into the network by the ends of the molecules of rubber diminish the effective number of cross-linkages. The theoretically derived factor which expresses this dependence on initial molecular weight is in good agreement with experiment.

The swelling capacity of vulcanized rubber in solvents, like the elastic modulus, is related to the number of effective cross-linkages. Hence, modulus and swelling capacity can be related to one another. The equation expressing this relationship is amply confirmed by experimental results. From this it is concluded that the same cross-linkages are effective in the presence of solvents which swell the rubber as are operative in the reaction of the rubber to elastic deformation.

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