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Stress-Strain Relation of Pure-Gum Rubber Vulcanizates in Compression and Tension

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The stress-strain curve in tension for a typical pure-gum rubber vulcanizate after a given period of creep, according to Martin, Roth, and Stiehler, can be represented by an empirical equation

$$F=M(L^{-1}-L^{-2})\exp A(L-L^{-1})$$

where F is the stress based on the original-cross sectional area, and L is the ratio of stressed to unstressed length, M is the slope of the stress-strain curve at $L=1$ and A normally has a value close to 0.38. The present paper shows by an examination of data published by Sheppard and Clapson, Treloar, and Rivlin and Saunders that the equation is also valid in the region of compression for values of L as small as 0.5 (50 percent compression). The features of the empirical equation are discussed, and comparisons are made with the equation predicted by the statistical theory of rubber elasticity and the equation derived by assuming Hooke's law for the stressed cross section. The consequences of the validity of the empirical equation in terms of the Mooney-Rivlin presentation of the strain energy function are pointed out. The equation predicted by the statistical theory represents observed data very well in the compression region from $L=0.5$ to $L=1.0$. The Mooney equation is approximately valid from $L=1.5$ to $L=3.5$. Neither of these equations is satisfactory in the important intermediate region from $L=1.0$ to $L=1.5$. The empirical equation represents the observed data over all three of these regions. It is concluded that Young's modulus M can best be obtained from the intercept of a plot of log $F/(L^{-1}-L^{-2})$ against $(L-L^{-1})$. For $0.75<L<2.00$ it is thoroughly satisfactory to determine M as the intercept of a plot of $F/(L^{-1}-L^{-2})$ against $(L-1)$.

1. Introduction

The stress-elongation curve of a typical pure-gum rubber vulcanizate after a given period of creep, according to recent work of Martin, Roth, and Stiehler [1],[1] can be represented up to 200 percent elongation or more by an empirical equation

$$F=M(L^{-1}-L^{-2})\exp A(L-L^{-1}) \quad (1)$$

where F is the stress based on the original cross-sectional area, L is the ratio of stressed length to unstressed length, and M and A are constants. M is Young's modulus, the slope of the stress-elongation curve at zero stress (where $L=1$). A normally has a value close to 0.38.

A graph of F/M against L as computed from eq (1) is given by the solid line of figure 1, reproduced from a recent review [2]. Although the range of conditions of applicability of eq (1) has not been thoroughly explored, Martin, Roth, and Stiehler [1] showed it to be valid for the first extension of pure-gum vulcanizates of natural rubber, GR–S, GR–I, and Neoprene over a 10-fold range of times of vulcanization and for constant times of creep from 1 to 10,000 min. It was found not applicable to vulcanizates containing carbon black or other fillers.

The investigations of Martin, Roth, and Stiehler were limited to specimens in simple tension. Consequently it was considered to be of interest to determine whether the same empirical equation can be applied to the compression region. The present paper shows from data already published by Sheppard and Clapson [3], Treloar [4], and Rivlin and Saunders [5], that, until the compression exceeds about 50 percent ($L=0.50$), the equation is valid with the same constants that apply in the extension region.

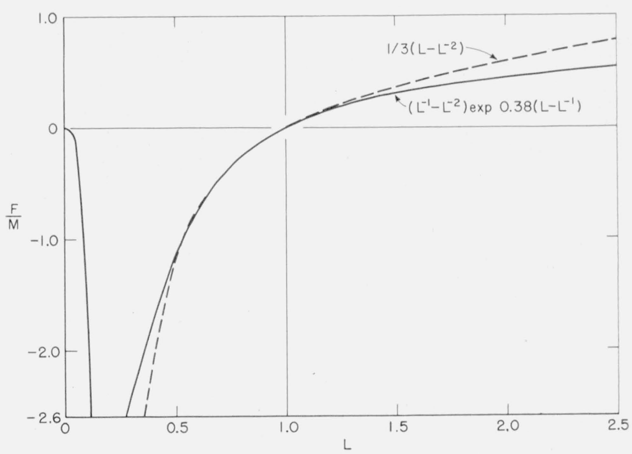

FIGURE 1. *Relation between stress-modulus ratio F/M and length ratio L.*

Solid line: empirical function $(L^{-1}-L^{-2})\exp 0.38(L-L^{-1})$. Dashed line: statistical theory function $(1/3)(L-L^{-2})$.

2. Compression and Tension Data

The friction that arises when compressional forces are applied to a flat specimen is a major source of experimental difficulty. It was pointed out years ago by Sheppard and Clapson [3] that a system fully equivalent to friction-free compression with freedom of displacement normal to the compressive force is obtained by subjecting a sheet to two-dimensional stresses in the plane of the sheet while

[1] Figures in brackets indicate the literature references at the end of this paper.

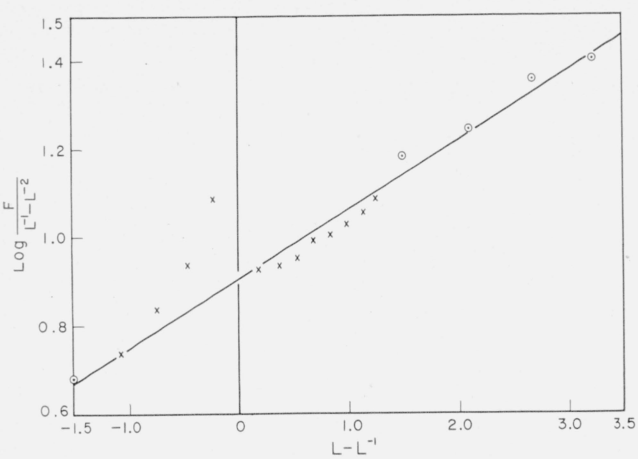

FIGURE 2. *Determination of constants in empirical equation from plot suggested by eq (1).*

×, Data from figure 10 of Sheppard and Clapson [3]; ⊙, data from figure 9 of Sheppard and Clapson [3].

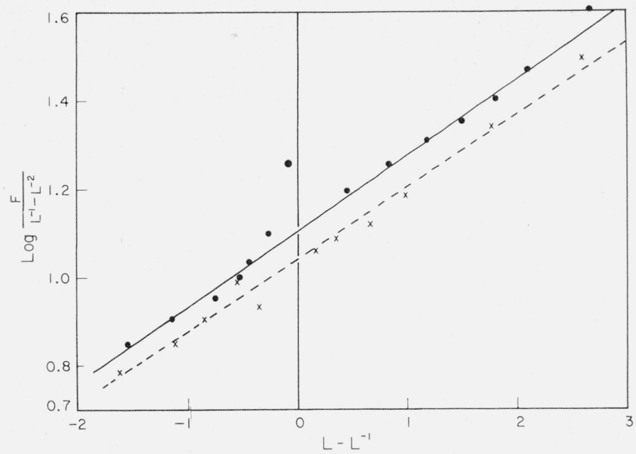

FIGURE 3. *Determination of constants in empirical equation from plot suggested by eq (1).*

●, Data of Treloar [4]. ×, Data of Rivlin and Saunders [5].

allowing freedom of displacement in the direction normal to the sheet. Data obtained by studying the relation between deformation and inflation pressure in balloons were presented by these authors. Values obtained on both compression and tension shown in figures 9 and 10 of the paper by Sheppard and Clapson [3] have been read from the figures to obtain log $F/L^{-1}-L^{-2}$) and $(L-L^{-1})$, the quantities necessary for checking the validity of eq (1). They have been plotted as co-ordinates in figure 2 of the present paper. It has already been pointed out [1] that such a plot in the tension region should yield a straight line with A as slope and log M as intercept. The linearity of the plot shown here covering both compression and tension seems quite satisfactory. Sheppard and Clapson themselves have called attention to the probable inaccuracy of the two points obtained at the smallest value of compression (where $L=0.8$ and 0.9). The values of A obtained from the plot in figure 2 is 0.36 in close agreement with values found by Martin, Roth, and Stiehler [1]. The value for log M of 0.91, corresponding to a Young's modulus of 8.1 kg/cm^2, is quite reasonable for a "cold-cured" balloon rubber. It is presumed that the vulcanizing agent was sulfur chloride.

The upper curve of figure 3 represents data from the work of Treloar [4], who made measurements similar to those already described but used a vulcanizate compounded with 8 parts of sulfur per hundred parts of rubber. The data in the compression region are taken from Treloar's table 1. For the points corresponding to compression ratios of 0.80, 0.77, and 0.69 the values of the equivalent compressive force were taken as 3.39, 3.89, and 5.82 kg/cm^2, respectively, after correcting an apparent typographical error in Treloar's table 1. Values in the tension region were read from figures 3 and 5 of Treloar's paper.

For values of L greater than 0.5 the experimental points lie quite close to the straight line drawn in figure 3, with the exception of the point for $L=0.95$. The value of A obtained from this plot is 0.394, in satisfactory agreement with previous work [1]. The value for log M of 1.1 corresponds to a Young's modulus of 12.7 kg/cm^2, nearly the same as the value, 12.0 kg/cm^2, taken by Treloar to represent the data in the compression region and up to about 30 percent elongation.

The lower curve of figure 3 represents data from the work of Rivlin and Saunders [5], whose measurements were similar to those of Treloar. The rubber was a conventional sulfur vulcanizate accelerated with benzothiazyl disulfide (MBTS). The data in the compression region were taken from table 8 of the paper by Rivlin and Saunders, while the data in the tension region were read from figure 14 of their paper. Values of $A=0.382$ and $M=11.1$ kg/cm^2 are obtained from figure 3.

It will be noted that in 2 of the 3 sets of data in figures 2 and 3, the values of the ordinate lie increasingly above the straight line as L approaches 1 in the compression region. It is possible that this represents a significant characteristic or it may be that it was due to residual stresses or other nonisotropic phenomena. Martin, Roth, and Stiehler [1] also reported instances of apparent high values near L=1 for certain vulcanizates in the tension region. However, in the present paper we shall neglect the possibility that the observation is significant since better data in the region near $L=1$ would be required to establish a definite conclusion of this sort.

It is concluded from figures 2 and 3 that eq (1) provides a satisfactory representation of the stress-strain relation for compressions less than 50 percent (i. e., for L greater than 0.5), and for elongations up to about 250 percent (i. e., $L=3.5$).

3. Features of the Empirical Equation

The solid line in figure 1, depicting the values of F/M computed from eq (1) with $A=0.38$, includes both compression and tension regions. The descending portion, beginning at the origin, of course has no physical significance. A minimum value of $F/M=-3.3$ at $L=0.18$ is followed by the rising portion shown. A point of inflection (corresponding to a maximum slope) at $L=0.26$ is followed by a steady decrease of slope, passing through unit slope at $L=1$, until another point of inflection (corresponding to a minimum slope) is reached at $L=2.91$. As pointed out in the preceding sections, the equation represents the experimental data reasonably well over the interval from $L=0.5$ to about $L=3.5$.

One can find two approximations to eq (1) that are useful over limited regions. The exponential term in eq (1) can be expanded in a power series. If only the first two terms of the series are retained and a reciprocal term is approximated [1], the following equation is obtained:

$$F/M=[L^{-1}-L^{-2}][1+2A(L-1)] \tag{2a}$$

or

$$F/M=2A-(4A-1)L^{-1}-(1-2A)L^{-2}. \tag{2b}$$

For $A=0.38$ this becomes

$$F/M=0.76-0.52L^{-1}-0.24L^{-2}. \tag{3}$$

This equation approximates eq (1) within about 0.5 percent over the range from $L=0.75$ to $L=2.0$. The compensating effect of some pairs of terms neglected in the expansions makes the approximation better than would be expected at first glance.

In the range above $L=2$ the empirical function is nearly linear over considerable region. A useful approximation here is

$$F/M=0.164L+0.125. \tag{4}$$

Values computed from eq (4) differ from values given by eq (1) by less than 4 percent from $L=2$ to $L=4.5$. The upper limit given is above the normal range of validity of eq (1).

4. Equation Predicted by Statistical Theory

The dashed line in figure 1 shows the function

$$F/M=(1/3)(L-L^{-2}) \tag{5}$$

predicted by the statistical theory of rubber elasticity [2, 6, 7] for the entropy component of the "equilibrium" stress of an ideal network. The agreement between the two functions in the region between $L=0.5$ and $L=1$ is quite striking. Calculation of numerical values shows that the difference is less than 4 percent throughout this interval. Since the precision of the available compression data is no better than this figure, no statement can be made as to which function conforms better to experimental observations in this region.

This agreement, together with the conclusion of Treloar [4] that eq (5) adequately represents his experimental data in this region, confirms the validity of eq (1) here, as already demonstrated directly by figures 2 and 3. Recent direct measurements of compression of specimens with lubricated surfaces by Forster [8] have also shown conformity to eq (5) or eq (1) from $L=0.67$ to $L=1$.

In the region of tension, however, the difference between the two functions becomes steadily greater as L increases. The value of $(1/3)\ (L-L^{-2})$ is about 4 percent greater than that of the empirical function at $L=1.15$, about 32 percent greater at $L=2.0$, and about 57 percent greater at $L=3.0$. These differences preclude the use of eq (5) for values of L above about 1.15. The slope of the graph of $(1/3)\ (L-L^{-2})$ against L approaches 0.333 as L is increased; the slope of a similar graph of the empirical function is 0.164 for a considerable region beyond $L=2$, as shown by eq (4).

Equation (5) is intended to apply to the entropy component of the stress of an ideal network of permanent cross links under "equilibrium" conditions. Equation (1), on the other hand, represents experimental values of stress obtained on conventional pure-gum vulcanizates after a fixed period of creep. Most, if not all, of the divergence between the two equations is to be ascribed to these differences. In the case of natural rubber at least, the divergence is associated with the entropy and can not be ascribed to changes of internal energy on stretching [2].

The observations are consistent with the representation of a conventional pure-gum vulcanizate as a network differing from the ideal network in having labile cross links that disappear during extension, the number disappearing increasing slightly with time at a fixed elongation and increasing considerably with increasing elongation at a fixed time. The cross links which have disappeared reform in time if the elongation is reduced. The data would indicate that the cross links are not affected by moderate compression. Such a network would be similar to an actual vulcanizate in showing creep in tension and a stress-modulus ratio increasingly less than the ideal as the elongation increases.

5. Equation Assuming Hooke's Law for Stress on Deformed Section

Another equation that has often been suggested for representing the stress-strain curve is obtained by assuming the constancy of Young's modulus M with the stress based on the stressed cross section. The result is

$$F/M=1-L^{-1}. \tag{6}$$

Calculation shows that this function is not at all satisfactory in the compression region. This function yields values about 11.5 percent less in absolute magnitude than the empirical function at $L=0.5$ and the difference falls below 4 percent when L is greater than 0.85.

In the region of tension eq (6) gives a value about 4 percent greater than that given by eq (1) at $L=1.18$. The difference has a maximum of about 13.2 percent at $L=2.2$ and falls to 9 percent at $L=3$.

It is clearly inaccurate to assume the validity of eq (6) up to about $L=2$, as has been done by some previous workers. If one should attempt to represent observations in the tension region by assuming an apparent modulus 6.6 percent less than M, positive and negative differences of about 6.6 percent would be obtained between the values from eq (6) and those observed. In the compression region, however, the differences would be increased by about 6.6 percent to become as great as about 18 percent at $L=0.5$. This is not a satisfactory representation of the observed data, which are given by eq (1) within the experimental accuracy of the observations discussed.

6. Mooney-Rivlin Equation

The work of Mooney [9] and Rivlin [5, 6, 7, 10] leads to an equation which may be written in the case of simple compression or tension, as

$$F/2=S_1(L-L^{-2})+S_2(1-L^{-3}) \tag{7}$$

where S_1 and S_2 are, in general, functions of L. In a region where Mooney's assumptions are valid S_1 and S_2 have constant values C_1 and C_2, respectively.

If one wishes to put eq (7) into a form suitable for a convenient plot he has two choices, suggested by the following two modifications of the equation:

$$\frac{F}{2(L-L^{-2})}=S_1+S_2L^{-1} \tag{8}$$

$$\frac{F}{2(1-L^{-3})}=S_1L+S_2 \tag{9}$$

More general relations are obtained by dividing both sides of each equation by M, the slope of the stress-strain curve at $L=1$.

$$\frac{F}{2M(L-L^{-2})}=\frac{S_1}{M}+\frac{S_2}{M}L^{-1} \tag{10}$$

$$\frac{F}{2M(1-L^{-3})}=\frac{S_1}{M}L+\frac{S_2}{M}. \tag{11}$$

Figure 4 shows a plot of Φ defined as $F/[2M(L-L^{-2})]$ against L^{-1} when F is obtained from the empirical equation, eq (1), giving A the value of 0.38. Correspondingly figure 5 shows a plot of θ defined as $F/[2M(1-L^{-3})]$ against L also utilizing eq (1). It will be noted, of course, that the compression regions appear on opposite sides of the value corresponding to $L=1$ in the two plots. From the equations it is obvious that the slope of the curve in figure 4 at any point is the intercept of the tangent to the curve of figure 5 at the corresponding point and vice versa. Furthermore it can readily be shown from their definitions that at $L=1$ both Φ and θ have the same value, namely 1/6, and that this value is independent of the form of the stress-strain relation. Consequently from eq (10) or (11) it is clear that $M=6(S_1+S_2)_{L=1}$.

It will be noted from figures 4 and 5 that no portions of the curves are linear for any extended range. However, over the range from $L=0.5$ to $L=1$ the values of Φ and θ are in reasonable agreement with the prediction of the statistical theory of rubber elasticity which would set $S_1/M=0.1667$ and $S_2/M=0$. The actual value of S_1/M, as calculated from eq (1), falls from 0.223 to 0.1267 in the range mentioned, while the value of S_2/M rises from -0.03 to $+0.04$. The average values over the range may well be taken as those predicted by the statistical theory. It will be noted, as already mentioned, that both the statistical theory and the empirical function require that at $L=1$ $\Phi=\theta=S_1/M+S_2/M=0.1667$.

Figures 4 and 5 show that over a range from perhaps $L=1.5$ to about $L=3.5$ the values of Φ and θ fall

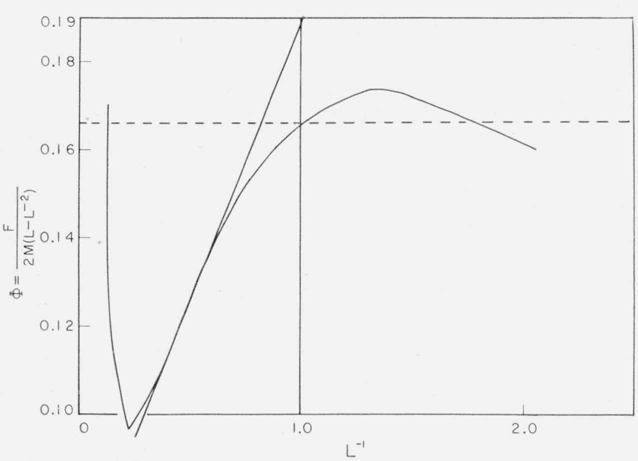

FIGURE 4. *Values of Φ obtained from empirical eq (1) in plot suggested by the Mooney-Rivlin Equation in the form of eq (10).*

Dashed straight line shows result predicted by statistical theory. Solid straight line shows result predicted by Mooney equation with constants C_1 and C_2 determined from region where $1.5<L<3.5$.

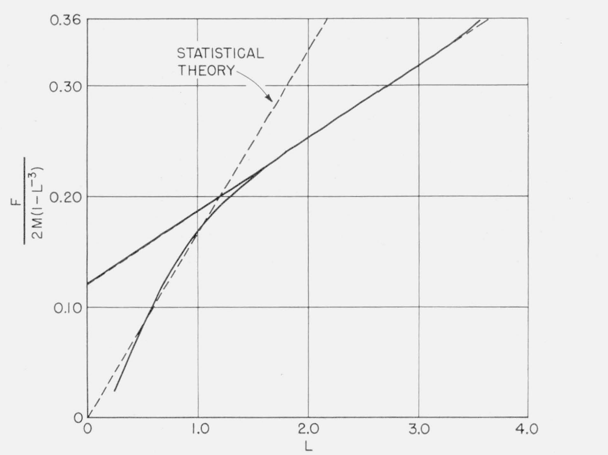

FIGURE 5. *Values of θ obtained from empirical eq (1) in plot suggested by the Mooney-Rivlin Equation in the form of eq (11).*

Dashed straight line shows result predicted by statistical theory. Solid straight line shows result predicted by Mooney equation with constants C_1 and C_2 determined from region where $1.5<L<3.5$.

approximately on a straight line in accordance with the prediction of the Mooney eq (9) calling for the constancy of S_1/M and S_2/M. It is clear that this is only an approximate constancy arising from the fact that the value of S_1/M passes through a minimum in this region, at a point of inflection of each curve, while the value of S_2/M is correspondingly passing through a maximum. Values of S_1/M and S_2/M at this point of inflection may be read from the solid lines of figures 4 and 5, but may be obtained more accurately by computation from eq (1). The values obtained by either procedure are $[S_1/M]_{min}=0.064$ and $[S_2/M]_{max}=0.124$. These values correspond to $L=2.3-2.4$. A straight line corresponding to a larger value of S_1/M and a smaller value of S_2/M would approximate the functions Φ and θ over a slightly larger range of values of L at the expense of accuracy of representation of the functions.

Over the important intermediate range for L between 1.0 and 1.5, however, neither statistical theory nor Mooney equation can satisfactorily represent Φ and θ, as shown in figures 4 and 5. Instead, S_1/M decreases continuously from 0.1267 to 0.08 in this transition interval while S_2/M increases continuously from 0.04 to 0.096.

A number of previous workers [11 to 16] have evaluated the Mooney constants C_1 and C_2 from stress-strain observations in tension, largely between $L=1.1$ and $L=2.0$. Almost all the specimens used differed considerably in degree of vulcanization from those for which eq (1) has been shown to be valid. Even more significantly, most of the measurements were apparently made after a prescribed procedure of prestretching and recovery, whereas the other observations mentioned up to this point were made with specimens stretched for the first time. From plots of the type suggested by eq (8) it was concluded [11 to 15] that C_2 had a value of approximately 1.03 kg/cm^2 for pure-gum vulcanizates containing sulfur and an accelerator. Under the same conditions C_1 had values ranging from about 1.0 to 3.0 kg/cm^2. Among more than 25 values given in these papers [11 to 15] there are only two instances where the same compound was investigated at different times of cure. In one case [11] covering 12, 15, and 17 min of cure C_1 increased ,C_2 decreased, and their sum increased slightly with increasing cure; in the other case [12] with cures of 10 and 30 min C_1 and the sum increased, but there was little change in C_2.

Blackwell [16] using plots of the type suggested by eq (9) obtained values for C_2 of about 0.8 kg/cm^2 and for C_1 of about 1.25 or 1.55 kg/cm^2 depending on the kind of rubber, but showing no variation with time of cure. It appears, from an examination of the conditions employed, that even at the shortest time of cure his vulcanizates had already reached a point where little change of modulus would be expected.

It is clear that under the experimental conditions employed by these workers, the value of C_2/C_1 is smaller than $0.124/0.064=1.94$ as given by the empirical function. As a result the size of the transition interval (in which S_2 increases from zero to a nearly constant value) is smaller than that given by the empirical function. The reason for the discrepancy is not clear but it is probably related to the very high degree of vulcanization and the previous mechanical history of the specimens employed by the British workers, as contrasted with those used by Martin, Roth, and Stiehler [1] and the observers whose results are given in figures 2 and 3.

In any case, unless Φ and θ show a sharp discontinuity in slope exactly at $L=1$, a transition interval must exist and must lie in the region of low elongations. Consequently linear extrapolation of tension data to $L=1$ is not justified in the region of low elongations in plots similar to figures 4 and 5. It may be concluded that the Mooney equation is not valid in the region of low elongations, since S_1 and S_2 show no approach to constancy in this region. Some of the implications of this conclusion in terms of the strain energy function have been pointed out in a recent review [2].

Thomas [17] has applied a correction term to the stress predicted by the statistical theory. Although this operation yields a graph of Φ qualitatively similar to figure 4 the stress-strain relationship predicted by Thomas's work departs so markedly from the solid line shown in figure 1 that the correction can not be regarded as satisfactory.

7. Young's Modulus from Experimental Observations

It is often a matter of considerable theoretical and practical importance to obtain a value of Young's modulus M from experimental observations of stress at one or more finite strains.

Since M is defined as the slope of the graph of F against L at $L=1$, the simplest method of determining its value would be to draw a tangent to the curve at this point and measure its slope. For values of L greater than 0.5 a plot of observed values of stress F against L will have the shape given by the solid curve of figure 1; the ordinates will simply be those shown, multiplied by the constant factor M. It can be seen from figure 1 that the curvature at $L=1$ is so great that the simplest method would not be very satisfactory. The tangent would be determined mainly by a few observations near $L=1$ where the experimental precision is not high.

Equations (1), (2a), (5), and (6) each represent satisfactorily the observed values of F in the region very near $L=1$, but differ in their ranges of applicability. Each equation can be put into such a form as to suggest coordinates that will give a linear plot near $L=1$, from which M may be obtained. Since eq (1) represents the data over a greater range than any of the others, a plot based on it can include a greater range of experimental observations than any of the others. The most satisfactory coordinates for a plot based on eq (1) are $\log F/(L^{-1}-L^{-2})$ and $(L-L^{-1})$, as illustrated by figures 2 and 3, where $\log M$ is obtained as the intercept. If only tension

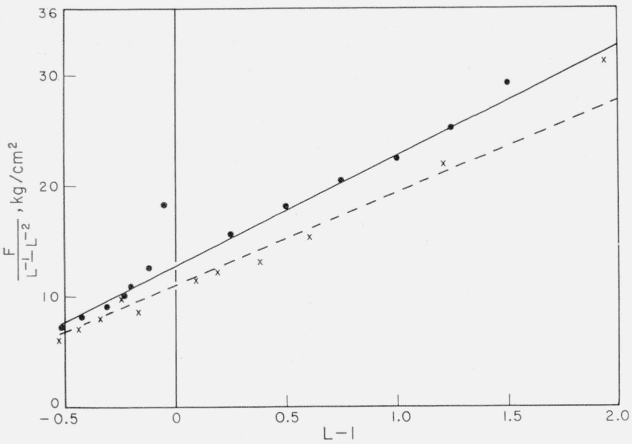

FIGURE 6. *Determination of constants in empirical eq (1) from plot suggested by approximation given as eq (2a).*

●, Data of Treloar [4]. ×, Data of Rivlin and Saunders [5].

data or only compression data are available this represents an extrapolation, but if data in both regions can be plotted, as in figures 2 and 3, the advantages of interpolation can be realized. A plot of this form shows by its linearity whether eq (1) is valid for the particular observations concerned and, if it is linear, its slope gives the value of A. Even if the plot should not be linear, the procedure of obtaining log M by interpolation should be satisfactory.

If the range of observations is not too great, a plot based on the approximation given by eq (2a) can be made. It can be seen that a plot of $F/(L^{-1}-L^{-2})$ against $(L-1)$ should yield a straight line with intercept M and with slope $2AM$. This is a thoroughly satisfactory procedure for observations between $L=0.75$ and $L=2.0$ since the approximation represents eq (1) within 0.5 percent over this region. Figure 6, showing this type of plot for the data of Treloar [4] and Rivlin and Saunders [5] may be compared with figure 3 showing the applicability of eq (1) to the same data.

Under conditions where the validity of eq (1) with $A=0.38$ may be reasonably presumed, M may be calculated from the equation, using a single observation of stress and the corresponding strain. If a repetition of the calculation with other observed values gives a constant value for M within experimental error, the validity of the equation is confirmed and the average obtained by such calculations may be taken as the desired Young's modulus.

The equation predicted by the statistical theory of rubber elasticity, eq (5), in spite of its disagreement with observed values in the tension region, has been frequently used to determine M. Since values of F/M predicted by this equation in this region are systematically too high as noted in figure 1, the calculated values of M are systemically too small by the amounts indicated in section 4, unless the results are extrapolated in some manner to $L=1$. The simplest graph based on eq (5) calls for a plot of F against $(L-L^{-2})$ for a determination of M from the slope. This procedure has been followed in recent work of Charlesby and von Arnim [18] on rubber cross linked by radiation. Unlike the conventional vulcanizates considered in the present paper, this material appears to conform to eq (5) up to high elongations. A similar method employed by Bueche [19] requires a plot of FL^2 against L^3 for a determination of M by extrapolating the observed slope to $L=1$.

A more sensitive method than either of these is to plot $F/(L-L^{-2})$ against L as in the work of Gee [20] or against L^{-1} as in other work [5, 11 to 15, 21]. These graphs should have the constant value $M/3$ where the statistical equation is applicable. This has indeed been found true [4, 8] in the compression region for L between 0.1 and 1. In the tension region, however, the value is not constant, and a linear extrapolation to $L=1$ is not justified, as already mentioned. Figure 4, differing from the latter plot only by two constant factors, shows the curvature to be expected near $L=1$.

The following modifications of eq (6)

$$F=M(1-L^{-1}) \tag{12}$$

and

$$FL=M(L-1) \tag{13}$$

show that straight lines of constant slope M would result from a plot of F against $(1-L^{-1})$ or of FL against $(L-1)$, if Hooke's law based on actual section were valid. It has been shown in section 5 that values of F/M obtained on this assumption are about 4 percent too high at $L=1.18$. If greater accuracy than this is desired, the slope must be obtained from lower values of L. The use of eqs (12) and (13) for L between 1.0 and 1.1 is a reasonably satisfactory approximation since the value of F/M obtained is less than 2.5 percent too great in this region. Baldwin, Ivory, and Anthony [22] have obtained linear plots of eq (13) for pure-gum vulcanizates of nitrile rubber and GR–I in this region.

Considerations outlined more fully in the section on the Mooney-Rivlin equation show that M can be obtained by determining the value of $F/2(L-L^{-2})$ or the value of $F/2(1-L^{-3})$ at $L=1$ since these quantities both are equal to $M/6$ at this point. If these operations are done graphically, curves similar to figures 4 and 5 are obtained, except that the ordinates are multiplied by a constant factor. It is clear that the curvature in the region of low elongations is so great as to make satisfactory extrapolation quite difficult.

In summary, Young's modulus M can best be determined from the intercept of a plot like figure 2 or 3, based on eq (1). This will permit the utilization of observations over the widest possible range of values of L in compression and tension. A plot like figure 6, based on the approximation given by eq (2a) is thoroughly satisfactory between $L=0.75$ and $L=2.0$. It is considerably superior to any of those based on eq (5), (6), or (7). The use of a plot based on eq (6) will give apparent values of M less than 2.5 percent too low if observations are confined to elongations of less than 10 percent. The use of a plot based on eq (5) will be satisfactory in the compression region and also will give apparent values of M less than about 2.7 percent too low if observations are confined to elongations of less than 10 percent. The use of a plot based on eq (7), differing only in scale from figure 4 or 5, is not satisfactory for obtaining M by extrapolation because of its large curvature in the region from $L=1.0$ to $L=1.5$.

8. Conclusions

The empirical function of Martin, Roth, and Stiehler [1] represented by eq (1) where A has the value of 0.38 may be regarded as an adequate representation of the available experimental data covering both the compression and tension of pure-gum vulcanizates. The stress and strain are to be measured after a constant time of creep. The approximate validity extends over the range $0.5<L<3.5$. The success of the single empirical function in representing data obtained in both compression and tension over a range as great as this is regarded as very significant.

In the range of values of L from 0.5 to 1.0 (compression) the empirical function gives results in agreement with the predictions of the statistical theory of rubber elasticity. After representing the stress and strain in a transition region extending from $L=1.0$ to 1.5, the empirical function gives approximately constant coefficients C_1 and C_2 in the Mooney equation over the range from 1.5 to about 3.5.

The behavior of the empirical function in the transition region from $L=1.0$ to $L=1.5$ shows that the statistical theory of elasticity fails to represent the experimental data even at the lowest elongations while proving satisfactory in the compression region. The Mooney-Rivlin equation also fails to furnish adequate representation of the experimental data at low elongations.

The most satisfactory method of determining Young's modulus from experimental observations of stress and strain in pure-gum vulcanizates involves a plot of log $F/(L^{-1}-L^{-2})$ against $(L-L^{-1})$. For observations within the range of $L=0.75$ to 2.0 the simpler plot of $F/(L^{-1}-L^{-2})$ against $(L-1)$ is thoroughly satisfactory. In both cases M is obtained from the intercept, and the constant A in eq (1) is determined from the slope.

WASHINGTON, September 16, 1957.

9. References

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