Studied in Rubber Elasticity. 1. An Alternative to the Mooney Equation

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ABSTRACT: Various equations for the stress–strain curve of a rubber in simple elongation are compared by making use of the reduced force $[f]$ as the quantity measured experimentally. All are expressible by the equation $[f] = \sum_\alpha g_\alpha F_\alpha$ where g_α is a modulus and $F_\alpha \equiv 2\alpha^{-1}(\lambda^\alpha - \lambda^{-\alpha/2})(\lambda - \lambda^{-1})^{-1}$. The Mooney equation involves two terms, with $\alpha = 2$ and -2, but has serious shortcomings. A new equation proposed to overcome these has three terms, $\alpha = 2$, 4, and 0, and is shown to fit a family of rubbers with the choice of parameters limited by the equations $g_4 = a_4 g_2^2$ and $g_0 = a_0 g_2^{1/2}$. The effect of swelling can also be predicted fairly satisfactorily. Some comments are made on the molecular significance of the terms in the new equation.

I. Introduction

The understanding of rubber elasticity is central to polymer science, and it is fortunate that a very simple statistical mechanical treatment of a crude model suffices to give a satisfying account of the main features of the experimental observations.[1] We represent the polymer by a group of randomly kinked chains linked together into a network, ignoring both its detailed topology and the problems which must arise from the physical entanglements between molecules. If a cube of side L_u in the rest state is deformed to a block having sides $\lambda_1 L_u$, $\lambda_2 L_u$, and $\lambda_3 L_u$, the simple theory predicts that the free energy will increase by

$$G_{el} = CL_u^3(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (1)$$

where

$$C = \tfrac{1}{2}FkT \quad (2)$$

F being a factor proportional to the number of chains in unit volume (see Section IXi). We ignore for the purpose of this paper the controversial additional term in ln $(\lambda_1\lambda_2\lambda_3)$.

Since the elastic free energy arises from deformation of the network, eq 1 applies to volume changes produced by swelling as well as to changes of shape resulting from mechanical stresses. We shall be concerned in particular with the uniaxial stretching at constant pressure and temperature of a sample which may be preswollen to a volume fraction of polymer equal to ϕ_2. If the stretched (swollen) length is L, we define the elongation ratio by

$$\lambda = L\phi_2^{1/3}L_u^{-1} \quad (3)$$

It then follows from eq 1 that the stretching force is given by

$$f = \left(\frac{\partial G_{el}}{\partial L}\right)_{P,T} = 2CL_u^2\phi_2^{-1/3}(\lambda - \lambda^{-2}) \quad (4)$$

It is convenient to react this equation in terms of the "reduced force", defined by

$$[f] \equiv \frac{f\phi_2^{1/3}}{L_u^2(\lambda - \lambda^{-2})} = 2C \quad (5)$$

Most of the experimental data on rubber elasticity derive from measurements of f vs. λ, and we shall examine them by enquiring what sort of deviations are observed from the predictions of eq 5 that $[f]$ should be independent of both λ and ϕ_2.

II. The Mooney Equation[2]

The best documented departure from eq 5 is the observed fall of $[f]$ as λ increases from 1 to 2. Many workers testify to the fact that a plot of $[f]$ against λ^{-1} is effectively linear in this range, i.e., that

$$[f] = 2C_1' + 2C_2'\lambda^{-1} \quad (6)$$

Apart from the primes on C_1 and C_2, this is the well-known Mooney equation, developed originally[3] from the empirical stored energy function (per unit volume).

$$W = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) \quad (7)$$

This equation was proposed by Mooney for its ability to represent the observed behavior both in simple elongation and in simple shear. For unswollen samples ($\phi_2 = 1$) it leads to eq 6 with $C_1' = C_1$, $C_2' = C_2$.

Although the Mooney equation provides an empirical description of the behavior of a *material*, it is plausibly argued that it must in fact describe the *network* deformation and should therefore be applicable to swelling as well as to mechanical deformation. If we assume this to be the case, it is easy to predict how C_1' and C_2' will depend on ϕ_2.

If C_1 and C_2 are the constants measured on the unswollen material, the prediction is:[4]

$$C_1' = C_1 \quad (8)$$

$$C_2' = C_2\phi_2^{4/3} \quad (9)$$

Thus the Mooney plots (eq 6) for a series of samples progressively swollen should show diminishing slopes but a constant intercept at $\lambda^{-1} = 0$. This is widely claimed to be confirmed by experiment, with the concentration dependence of C_2' given at least approximately by eq 9. Many workers build on this to make further claim that C_1' is to be identified with C of eq 5 and hence also of eq 2. C_1' has therefore been extensively used to estimate the concentration of chains in the network.[5]

Critical examination of the evidence reveals very serious objections to this attractively simple picture. If the Mooney plot is continued beyond the usual range large discrepancies appear.[6] At higher elongations $[f]$ goes through a minimum (typically about $\lambda^{-1} = 0.3$) beyond which it rises sharply. In compression $[f]$ is almost constant, with probably a flat maximum between $\lambda^{-1} = 1$ and 2. Thus the Mooney plot as normally presented is in truth no more than an approximately linear section of a more complex curve. (Examples are given later, in Figures 5 and 6.) Moreover, the effect of swelling is to move the position of the minimum and subsequently sharp rise to progres-

[‡] It is a privilege to dedicate this paper to my friend Paul Flory, who has made and continues to make so many important contributions to our understanding of rubber elasticity. My colleagues Colin Price and L. R. G. Treloar, who have helped me greatly by their comments during the preparation of this paper, wish to be associated in congratulations and good wishes.

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Table I

% of S	$[f]_1$, MN m^{-2}	α_1	μ_1, MN m^{-2}	α_2	μ_2, MN m^{-2}	α_3	μ_3, MN m^{-2}
2	0.4807	1.3	0.69	4.0	0.01	−2.0	−0.0122
3	0.3490	1.9889	0.3041	7.3258	1.74×10^{-5}	−1.3816	−0.0673
5	0.5042	1.2947	0.7525	4.7808	4.74×10^{-3}	−2.5505	−0.00449

sively higher values of λ^{-1}, until the "linear" portion almost disappears.[8] Finally, measurements in general biaxial strain are not satisfactorily described by eq 7.[9]

III. Equations Based on a Power Series

The shortcomings of the Mooney equation have stimulated a number of attempts to find empirically a more satisfactory stored energy function. One which has attracted attention in recent years[10] involves the generalization of eq 7 to the form

$$W = \sum_i \frac{\mu_i}{\alpha_i}[\lambda_1^{\alpha_i} + \lambda_2^{\alpha_i} + \lambda_3^{\alpha_i} - 3\,(\lambda_1\lambda_2\lambda_3)^{\alpha_i/3}] \quad (10)$$

in which it is sufficient for our present purpose to put $\lambda_1\lambda_2\lambda_3 = 1$. This equation is still consistent with the Valanis–Landel hypothesis[11] that W should be expressible as the sum of three independent functions of the principal extension ratios, i.e., that

$$W = \omega(\lambda_1) + \omega(\lambda_2) + \omega(\lambda_3) \quad (11)$$

Several workers, including especially Treloar and his coworkers,[12] have shown that measurements over a wide range of biaxial strain can be represented by using three terms. Their data were used to calculate the function $\lambda\,(\partial\omega/\partial\omega)$ which was then fitted to the expression, derived from (10) and (11),

$$\lambda\,(\partial\omega/\partial\lambda) - \text{constant} = \sum_i \mu_i(\lambda^{\alpha_i} - 1) \quad (12)$$

(The arbitrary constant arises from the assumption of incompressibility.) Table I shows the sets of parameters assigned[12] to three different specimens obtained by sulfur vulcanization of natural rubber. The second column gives the reduced force $[f]_1$ at $\lambda = 1$ calculated from $[f]_1 = {}^1/_2 \cdot \sum_i \alpha_i\mu_i$. Features to note in the table are (i) the wide spread of parameters and (ii) the dominant contribution to $[f]_1$ made by the first term.

The notable success of this equation in fitting a spectrum of experimental data is offset by two serious losses: (i) complete divorce from any molecular theory; (ii) inability to predict from measurements on one sample the behavior of another differing in cure or in swelling.

IV. Power Series with Restricted Choice

The purpose of this paper is to advocate the use of a three-term stored energy function obtained from eq 10 by restricting the values which may be assigned to the α_i. The problem of choice may be approached either empirically or by reference to molecular considerations. In developing our final equation both approaches have been used side by side, but for convenience of presentation we begin from an empirical standpoint, which follows naturally from the preceding sections.

Since most of the data available for comparison with any proposed equation are in the form of values of $[f]$ from elongation measurements, it is convenient to recast eq 10 in an essentially equivalent form. We define a function F_α by the equation

$$F_\alpha \equiv 2\alpha^{-1}(\lambda^\alpha - \lambda^{-\alpha/2})(\lambda^2 - \lambda^{-1})^{-1} \quad (13)$$

noting that $F_\alpha = 1$ when $\lambda = 1$. Attention may be called to four particular cases: $\alpha = 2$, $F_2 = 1$ (cf. statistical theory); $\alpha = -2$, $F_{-2} = \lambda^{-1}$ (cf. Mooney theory); $\alpha = 4$, $F_4 = {}^1/_2(\lambda^2 + \lambda^{-1})$; and $\alpha = 0$. Equation 13 becomes indeterminate, but F_α remains finite with the value $F_0 = 3 \ln \lambda(\lambda^2 - \lambda^{-1})^{-1}$ (eq 13[1]). We can now write an expression for $[f]$, derived from eq 10, in the form

$$[f] = \sum_\alpha g_\alpha F_\alpha \quad (14)$$

where the g_α are moduli and $\sum_\alpha g_\alpha$ is the reduced force at $\lambda = 1$. The curve fitting problem is to select three terms which together represent the observed behavior, including the sharp minimum at $\lambda^{-1} \sim 0.3$ and the flat maximum above $\lambda^{-1} = 1$, with the use of this equation. The nature of the problem is brought out by Figure 1, in which F_α is plotted as a function of λ^{-1} (for a range of values of α) to facilitate direct comparison with the Mooney plot of $[f] \sim \lambda^{-1}$. The solution now proposed was based on the following considerations. (i) $\alpha = 2$: This must certainly be the first term. Not only does this provide a link with the statistical theory, but as a curve-fitting device it gives us an adjustable constant term in eq 14. (ii) $\alpha = 4$: To provide an upturn at low λ^{-1} we must have a term with $\alpha > 2$. Our choice of $\alpha = 4$ is somewhat arbitrary, although we shall see later (Section IXii) that a molecular interpretation can be offered. (iii) $\alpha = 0$: We need a term to produce the observed slope between $\lambda^{-1} = 0.5$ and 1.0 without giving a large rise above $\lambda^{-1} = 1$. These two requirements conflict somewhat, though we note that the convexity of this plot in the usual Mooney region will be partly offset by the opposite curvature from the term $\alpha = 4$. The choice of $\alpha = 0$ is not considered critical, and it has not been thought necessary or desirable to explore the effect of small changes.

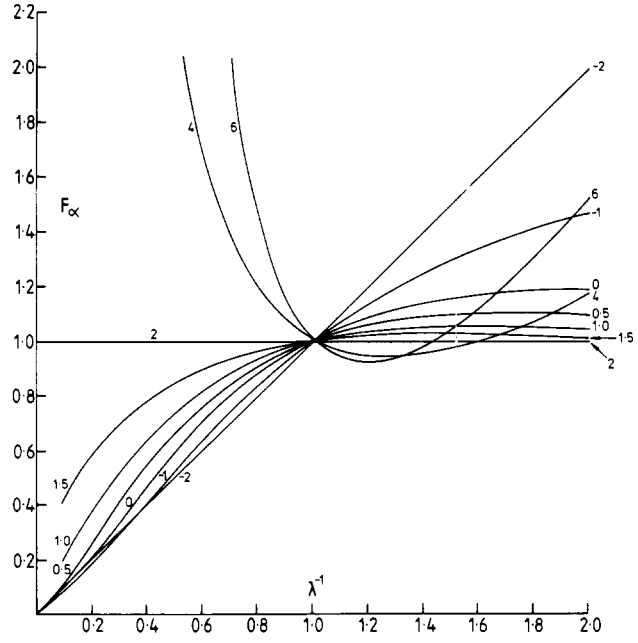

Figure 1. A graph of F_α as a function of λ^{-1} for values of α marked on the curves.

Our equation is therefore

$$[f] = g_2 + g_4F_4 + g_0F_0 \quad (15)$$

which combines with (13) to give

$$[f] = g_2 + {}^1/_2g_4(\lambda^2 + \lambda^{-1}) + 3g_0 \ln \lambda(\lambda^2 - \lambda^{-1})^{-1} \quad (16)$$

Table II

	g_2, M N m^{-2}	g_0, M N m^{-2}	g_4, M N m^{-2}
i	0.235	0.2335	0.0150
ii	0.215	0.272	0.0136

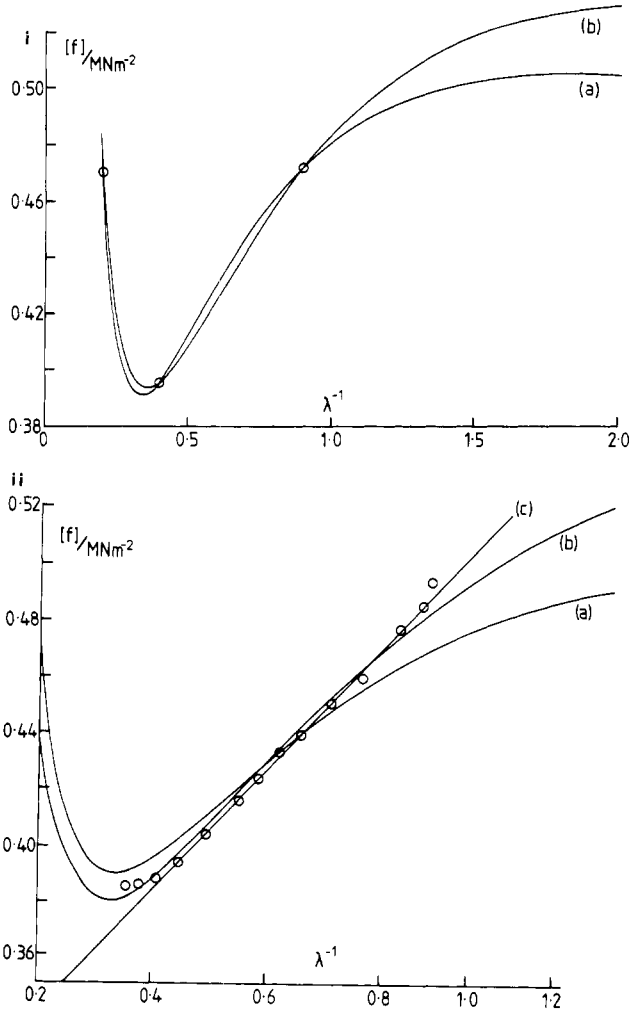

Figure 2. (i) A graph of $[f]$ (Jones and Treloar) as a function of λ^{-1}: (a) from Treloar's equation; (b) from eq 16 fitted to (a) at the three points marked. (ii) The same data as in (i). The points are experimental values. The curves are: (a) Treloar's equation; (b) eq 16 with revised constants; (c) the Mooney equation.

In the three following sections, we examine the usefulness of this equation in describing experimental results.

V. Comparison with Jones and Treloar's Equation

Equation 16 was fitted to the data of Jones and Treloar[12] in two ways: (i) Using the constants from Table I (2% S) to calculate $[f]$, we fitted eq 16 at $\lambda^{-1} = 0.2$, 0.4, and 0.9. (ii) The parameters were modified to give a better representation of the recorded measurements in the Mooney region. Table II lists the parameters and Figure 2i,ii respectively shows the fit obtained together in Figure 2ii with the Mooney line defined by $2C_1$(M N m^{-2}) = 0.294 and $2C_2$(M N m^{-2}) = 0.220.

The divergence from Jones and Treloar's curve nowhere exceeds 6% in the region $\lambda^{-1} = 0.2$–2. With three parameters to adjust, this measure of agreement is not very significant. A striking difference is found in the relative importance of the terms: eq 16 requires two comparable terms, whereas Jones and Treloar attribute 90% of $[f]_1$ to the term $\alpha = 1.3$. Reference to Figure 1 shows at once how this arises and why the Jones and Treloar curve is some way from being linear in the Mooney region.

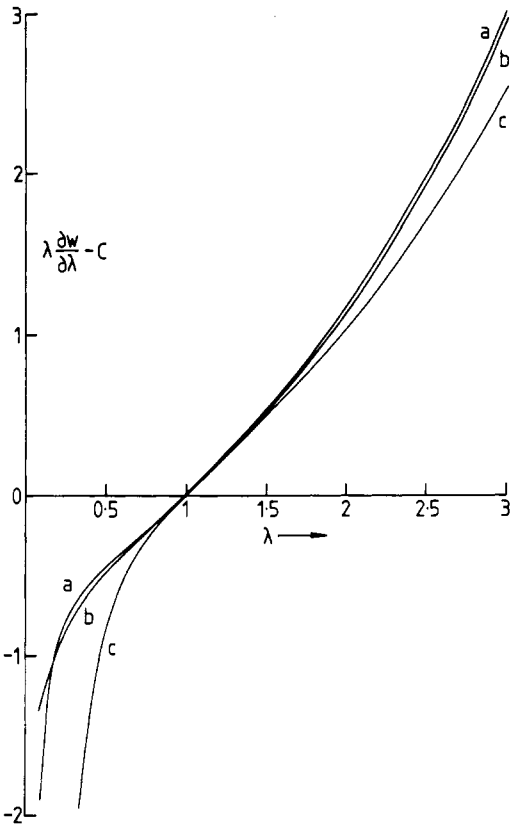

Figure 3. An alternative plot of data from Figure 2i + (c) from Figure 2ii extended to a wider elongation range (eq 12 and 17).

It is of interest also to investigate the possibility of extrapolation beyond the region to which eq 16 was fitted. In Figure 3 we therefore use Treloar's method of plotting by evaluating, from $\lambda^{-1} = 0.1$–3

$$\lambda\left(\frac{\partial\omega}{\partial\lambda}\right) - \text{constant} = g_2 + \tfrac{1}{2}g_4(\lambda^4 - 1) + 2g_0 \ln\lambda \quad (17)$$

Agreement is seen to be very close over most of the range, with large deviations only at very high deformations. It follows that our equation is capable of describing the behavior observed over modest degrees of biaxial strain. The equivalent curve (c) derived from the Mooney equation is seen to be seriously in error.

VI. Effect of Degree of Cross-Linking

Having selected values for α, the next step is to examine the properties of a family of similar rubbers differing only in the extent of cross-linking. Our equation would be of little value if the three moduli all have to be determined separately for each sample. A suitable body of data is found in the work of Mullins,[8] who studied the stress–strain behavior of five natural rubber compounds, cured by 1, 2, 3, 4, and 5% peroxide, and recorded measurements to a sufficiently high deformation to locate the minimum in $[f]$. This is of great help in determining the three moduli, since its position is dependent only on the ratio g_4/g_0 (Figure 4). In analyzing the data, the procedure first adopted was to treat each sample separately, but we found it difficult to determine three constants satisfactorily; the effect of changes in one constant could be offset by changes in the other two. A conspicuous feature of the family of curves is the systematic dependence of the minimum λ^{-1} on the degree of cross-linking. Using Figure 4 we found

Table III
Assignment of Parameters to Mullins Rubbers

rubber	peroxide concn, (P)/%	g_2, M N m^{-2}	$g_2(P)^{-1}$	g_4,[a] M N m^{-2}	g_0,[a] M N m^{-2}	$2C_1$, M N m^{-2}	$2C_2$, M N m^{-2}	$2C_1(P)^{-1}$
C-1	1	0.067	0.067	0.0037	0.171	0.087	0.173	0.087
C-2	2	0.118	0.059	0.0114	0.227	0.170	0.205	0.085
C-3	3	0.209	0.070	0.0358	0.302	0.373	0.179	0.124
C-4	4	0.233	0.059	0.0445	0.319	0.422	0.182	0.105
C-5	5	0.290	0.058	0.0690	0.355	0.528	0.197	0.106
		mean	0.063				mean	0.101

[a] Calculated from eq 18.

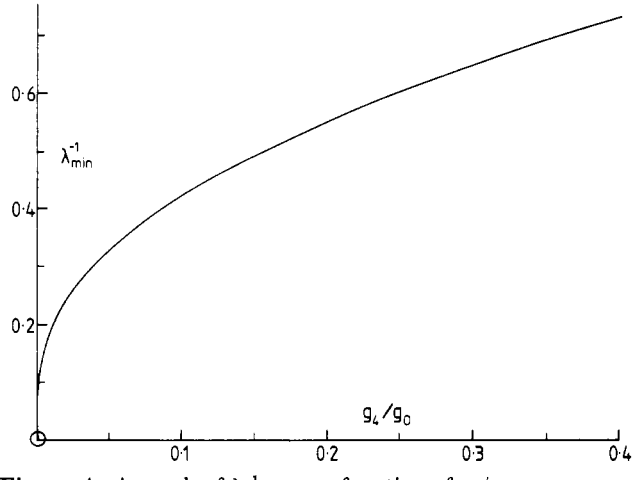

Figure 4. A graph of λ^{-1}_{min} as a function of g_4/g_0.

that, to a good approximation, $g_4/g_0 \propto (P)^{3/2}$, where (P) is the weight percentage of peroxide used in cross-linking. Furthermore, we may plausibly expect (from its formal relationship to the statistical theory equation) $g_2 \propto (P)$. Taking these two together, we were able to fit curves for the family of rubbers by assuming

$$g_4 = a_4 g_2^2 \qquad g_0 = a_0 g_2^{1/2} \tag{18}$$

All the experimental data could then be represented by

$$[f] = g_2 + \tfrac{1}{2}a_4 g_2^2(\lambda^2 + \lambda^{-1}) + 3a_0 g_2^{1/2} \ln \lambda(\lambda^2 - \lambda^{-1})^{-1} \tag{19}$$

with $a_0 = 0.66$ M N$^{1/2}$ m^{-1} and $a_4 = 0.82$ M N^{-1} m^2, where $[f]$ and g_2 are in M N m^{-2}. This leaves a single parameter g_2 adjustable for each sample. Table III shows the values assigned, and it will be noted that as expected g_2 is to a good approximation proportional to the peroxide concentration.

Figure 5 shows the experimental points for all five rubbers, with curves calculated from eq 19, with the use of g_2 values from Table III. A somewhat closer fit can be obtained by adjusting parameters separately for each sample, but the importance of Figure 5 is the demonstration of an acceptable fit to the whole group, using only a single parameter for each. Particularly satisfactory is the way in which the positions of the minimum are represented. This is of course outside the scope of the Mooney equation, although this can approximately represent the linear portions, taking these to be parallel (i.e., C_2 = constant) as can be judged from the values of $2C_1$ and $2C_2$ included in Table III. These were fitted individually to the data for the five samples.

VII. Properties of Swollen Materials

If the foregoing method of analysis is applied to a sample swollen (after cross-linking) to a rubber volume fraction

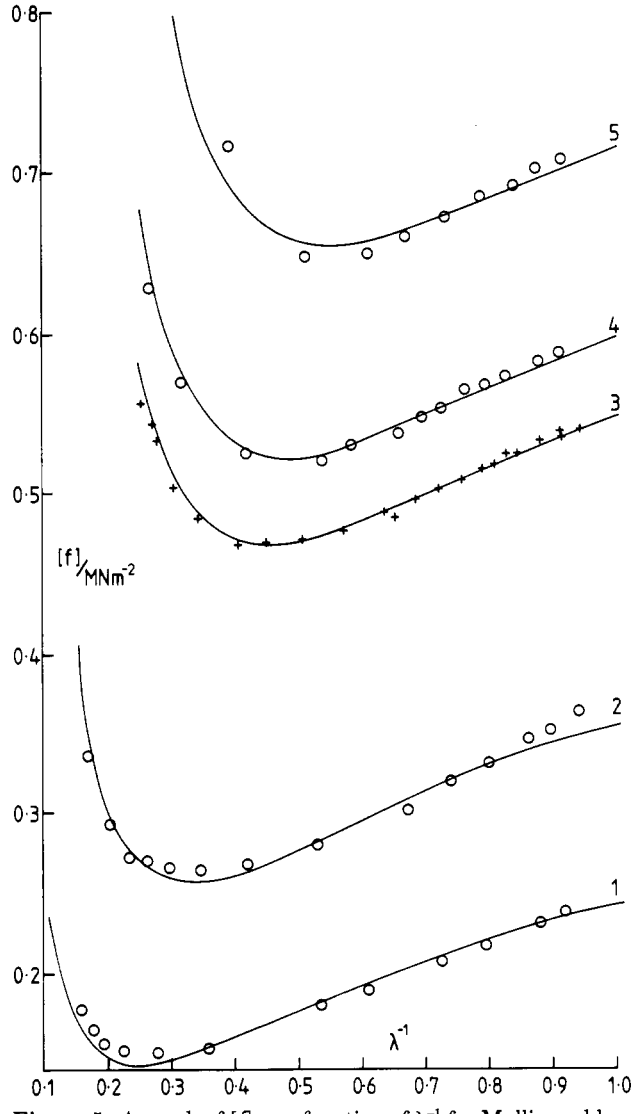

Figure 5. A graph of $[f]$ as a function of λ^{-1} for Mullins rubbers. The percent of peroxide is marked on the curves. The points are experimental values. The curves are from eq 19

ϕ_2, the volume dependence of the moduli is found to be $g_\alpha \propto \phi_2^{(2-\alpha)/3}$. Hence if a_0 and a_4 in eq 19 are given values appropriate to the unswollen rubber, the equation can be further generalized to:

$$[f] = g_2 + \tfrac{1}{2}a_4\phi_2^{-2/3}g_2^2(\lambda^2 + \lambda^{-1}) + 3a_0\phi_2^{2/3}g_2^{1/2} \ln \lambda(\lambda^2 - \lambda^{-1})^{-1} \tag{20}$$

Using this, we predict the behavior of swollen samples from measurements on the dry rubber. Figure 6 shows the result of doing this for the middle rubber of the five represented in Figure 5. Clearly the observed values lie consistently

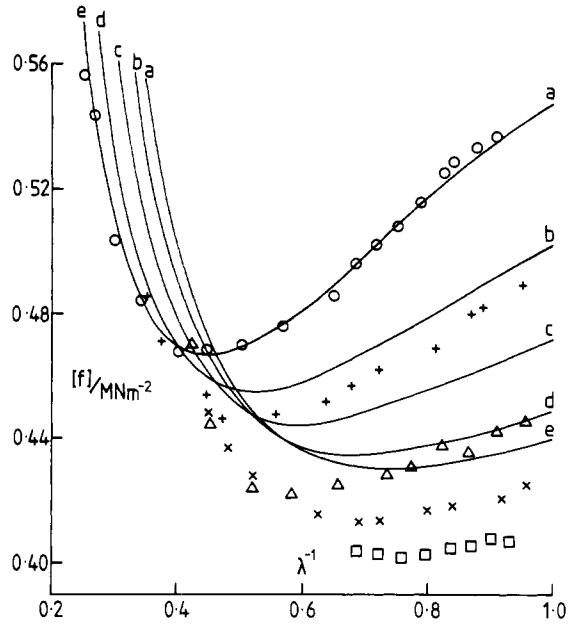

Figure 6. A graph of $[f]$ as a function of λ^{-1} for swollen rubbers. The points are experimental values. The curves are from eq 20, ϕ_2: curve a and ⊙, 1.000; b and +, 0.753; c and △, 0.585; d and x, 0.455; e and □, 0.407.

Table IV
Effect of Swelling on Reduced Force at $\lambda = 1$

	$[f]_1$, M N m^{-2}		
ϕ_2	obsd	eq 20	Mooney
1.000	0.558	0.558	0.552
0.753	0.502	0.513	0.496
0.585	0.455	0.481	0.461
0.455	0.434	0.457	0.436
0.407	0.417	0.449	0.427

below those calculated, but a very satisfactory feature is the way in which the progressive change of slope and shift of the minimum are predicted. Table IV compares values of $[f]$ at $\lambda = 1$ with those calculated (i) from eq 20 and (ii) from the Mooney constants of Table III. The Mooney equation is seen to give a somewhat better prediction but is of course unable to account for the shortening of the "linear" section.

VIII. Properties of Samples Cross-Linked in the Swollen State

A further body of data on the effect of a swelling agent refers to materials cross-linked in the swollen state and subsequently dried. When these are analyzed in terms of the Mooney equation, it is found that C_2 is generally much smaller than that for conventionally vulcanized samples.[13] Price et al.[14] have further reported, for natural rubbers vulcanized by peroxide, that C_1 is approximately proportional to $\phi_c^{2/3}$ where ϕ_c is the volume fraction at which cross-linking took place. The data are not sufficiently extensive to permit the evaluation of three constants, but it is clear that samples of low ϕ_c must require $[f] \approx g_2$ with g_0 and g_4 both small. It is easily shown that our method of analysis requires the result $g_\alpha \propto \phi_c^{\alpha/3}$, so we expect $g_2 \propto \phi_c^{2/3}$, $g_4 \propto \phi_c^{4/3}$, and g_0 = constant. The first two of these may well be consistent with observation; the third is certainly not, and the possible reason for this discrepancy must form part of our discussion of the $\alpha = 0$ term.

IX. Possible Molecular Interpretations

i. The $\alpha = 2$ Term. So far our approach has been largely empirical. In this section we consider briefly whether the three terms of eq 16 can be given molecular interpretations. We begin with the term involving $\alpha = 2$, chosen to give formal equivalence with the statistical theory result. The question to be posed now is whether g_2 can be related to the number of chains in the network. It is planned to consider this question at greater length in a further publication. Here we shall only compare values of g_2 for the five rubbers of Table III with the number of chains calculated from the amount of peroxide used. If we assume that each molecule of peroxide produces one cross-link and therefore links two chains, we find the number of chains in unit volume given by $\nu = 67(P)$ mol (chains) m^{-3}, where (P) is the weight percentage of peroxide used. This is certainly an overestimate, on two counts. First, experiments with different times of cure[8] show that cross-linking was probably about 70% efficient under the conditions used. Second, a correction is needed for network imperfections. A more realistic chemical estimate is therefore $\nu \simeq 45(P)$ mol (chains) m^{-3}. For comparison with this, we now postulate that g_2 is to be identified with the FkT of eq 2. It has already been noted (Table III) that g_2 is closely proportional to (P). Taking the average ratio, we find then $F = 25(P)$ mol (chains) m^{-3} and hence $F \simeq 0.55\nu$. For comparison, we observe from Table III that $2C_1(P)^{-1}$ is less satisfactorily constant than $g_2(P)^{-1}$. Using the mean of 0.101 and assuming the commonly made identification of $2C_1$ with FkT, we obtain the alternative estimate $F \simeq 0.9\nu$.

The relationship between F and ν has been much discussed. In a recent analysis, Flory[1b] has concluded that the ratio F/ν should lie between the limits 0.5 and 1, the lower bound being appropriate to a phantom network and the upper to one in which the motion of junction points is affine. It will be seen that either g_2 or $2C_1$ leads to a ratio lying within this band. Much more evidence is needed to carry the comparison further.

ii. The $\alpha = 4$ Term. There has been much discussion of the interpretation of the upturn in the reduced force at low λ^{-1}. Unquestionably such an upturn must occur eventually[15] as chains approach their maximum extension, when $[f]$ must tend to infinity. It has however been strongly argued[19] that what is seen experimentally is due to the onset of crystallization, occurring while the deformation is still adequately described by Gaussian statistics. Since all the data reviewed above refer to natural rubber, this argument cannot be lightly dismissed, but strong evidence against its importance is seen in the fact that swollen samples (which must be less ready to crystallize) reach their upturn at *lower* elongation. For the purpose of this paper we therefore look for an interpretation of the $\alpha = 4$ term entirely in terms of the finite extensibility of the chain.

The simplest analytical expression of departure from Gaussian statistics on high elongation of a random chain makes use of the inverse Langevin function[16]

$$f = \tfrac{2}{3}Cn^{1/2}[\mathcal{L}^{-1}(\lambda n^{-1/2}) - \lambda^{-3/2}\mathcal{L}^{-1}(\lambda^{-1/2}n^{-1/2})] \quad (21)$$

where n is the number of links in the random chain. According to this equation, $f \to \infty$ at $\lambda = n^{1/2}$. The leading terms in the series expansion for $\mathcal{L}^{-1}(x)$ are

$$\mathcal{L}^{-1}(x) = 3x + 1.8x^3 + \ldots \quad (22)$$

To this approximation eq 21 gives

$$f = 2C[(\lambda - \lambda^{-2}) + 0.6n^{-1}(\lambda^3 - \lambda^{-3}) + \ldots]$$

or

$$[f] = 2C + 1.2Cn^{-1}(\lambda^2 + \lambda^{-1}) + \ldots \quad (23)$$

If we put $2C = g_2 = 0.55\nu kT$ and $n v_1 = \nu^{-1}$ where v_1 is the

volume of a link, (23) becomes

$$[f] = g_2 + \frac{0.6}{0.55} g_2^2 \frac{v_1}{kT}(\lambda^2 + \lambda^{-1}) + \ldots \quad (24)$$

Comparing this with our empirical equation we see that (24) is of the form $[f] = g_2 + {}^1/_2 a_4 g_2^2(\lambda^2 + \lambda^{-1})$. Thus the choice of $\alpha = 4$ finds a molecular basis. Quantitative analysis of eq 24 is less satisfactory, the observed value of α_4 leading to $v_1 \sim 930$ cm^3 mol^{-1} and to values of n for Mullins' five rubbers ranging from 5 to 22. Undoubtedly this estimate of v_1 is too high and (equivalently) that of n is too low. The discrepancy stems, at least in part, from the fact that the series expansion (eq 22) does not converge rapidly for the elongation range of interest. Hence the term is $\alpha = 4$, while the logical first choice, must be expected to underestimate the non-Gaussian contribution at higher elongations.

iii. The $\alpha = 0$ Term. The third term differs from the other two in that no justification has been found from molecular considerations for its analytical form. The role of the Mooney C_2 in measuring departures from Gaussian behavior is here taken up by the ratio of g_0 to g_4. Nothing more than curve fitting led to the choice of $\alpha = 0$ and the subsequent relationship (over the range examined) $g_0 \propto g_2^{-2}$. Consequently the molecular interpretation of this term poses the same problem as that of C_2. Current thinking relates this to the contributions of entanglements or to the restrictions imposed on network configurations by the interpenetration of chains.[17] In developing this latter concept, Flory[18] has obtained a complex expression for the ratio between the tension f_c arising from constraints and that f_{Ph} arising from the phantom network.

With a suitable choice of the adjustable parameter in this equation, the plot of $[f]$ against λ^{-1} is very similar to that obtainable from an $\alpha = 0$ term (necessarily so, since both approximate to experiment). It is temptimg to look for equivalence between Flory's f_c/f_{Ph} and our g_0/g_2, but a quantitative discrepancy is observed between the theoretical limitation of the former to a value of 1 and the large values of the latter recorded in Table III. Quantitively the interpretation of g_0 as a measure of the restrictions imposed by chain interpenetration offers a ready explanation of the observation (Section VIII) that networks formed at high dilution have low values of g_0.

X. Conclusions

This paper has been entitled "an alternative to the Mooney equation". The Mooney equation has the virtue of simplicity but is applicable only to a restricted section of the stress–strain curve in simple elongation. Within this region the properties of a family of rubbers, swollen to different extents, are reasonably well described by eq 6 and 9, requiring one parameter for each rubber and one (C_2) for the family. The suggested alternative is eq 20, which again requires one parameter (g_2) for each rubber but two for the family. The gain is a much better account of the stress–strain behavior over a wide range, though marginally less good in the Mooney region $0.5 < \lambda^{-1} < 0.9$. The Mooney equation has been so widely used as to become an accepted basic tool. The suggested alternative, eq 20, is unproven. It must be tested on a much wider range of data before it can be claimed to provide a useful general equation. Its neglect of the effect of crystallization in determining the position of the minimum reduced force requires further study. The most important issue to be examined is the relationship of both equations to network structure. Current use of the Mooney C_1 as a measure of cross-linking is intuitive rather than rigorous. g_2 from eq 20 offers an alternative—equally intuitive. It is proposed to compare them more closely in a further publication.

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References and Notes

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