Studies in rubber elasticity: 2. Volume and energy changes in the elongation of elastomers

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The dilation which accompanies the elongation of an elastomer is related to the network stresses, and is therefore calculable from stress–strain behaviour. A systematic framework is outlined and used to compare a number of theoretical and experimental stored energy functions. Since none of these give fully satisfactory predictions of the observed dilation it is concluded that some additional source of volume change must exist. It is suggested that this is to be found in rotational isomerization and a correction proposed which gives greatly improved representation of dilation data. On this basis a two-parameter dilation equation is developed. Use of this leads to the conclusion that the correction needed to convert constant pressure thermoelastic data to constant volume is larger than currently calculated.

(Keywords: rubber elasticity; elastomers; dilation; energy changes; elongation; volume changes)

INTRODUCTION

I am very glad to take part in this tribute to the late Leslie Treloar. We became colleagues (in B.R.P.R.A.) in 1938 and for a number of years worked closely together. Our formal connection ceased when we both found new employment, but in recent years the proximity of our laboratories made it easy for us to exchange ideas. One aspect of the elastic behaviour of rubbers which continued to interest us both is the dilation which accompanies uniaxial deformation. When we published our joint paper[1] in 1950 it was recognized that dilation is a natural and necessary consequence of the stress system needed to produce simple elongation, but that its magnitude is so small (*ca.* 0.01% at 100% elongation) as to be difficult to measure. Subsequent experimental and theoretical work was reviewed by Price[2] in 1976 and by Treloar[3] in 1978. These reviews revealed unsolved problems in understanding quantitatively the measured dilation. The aim of this paper is to set these problems in a systematic framework and to offer a suggestion for their solution, and the first task is to find a general relationship between the dilation and the forces which produce it.

(1) THE PROBLEM

We consider the process in which a cube of material, of side L_u at temperature T and pressure P, is subjected to a uniaxial stretching force f, at constant T and P, as a result of which its length in the stretching direction becomes L and its volume V. The increase in free energy, often referred to as the 'stored energy' is denoted by Φ and we define the elongation ratio $\lambda = L/L_u$, the dilation $\Delta V = V - L_u^3$ and the dilation coefficient $Y = (\partial \ln V/\partial \lambda)_{P,T}$. It is to be noted that the available data fall within the range $1 < \lambda < 2$ and that $\Delta V/V$ does not exceed 2 or 3×10^{-4}. Some of the data to be discussed refer to samples pre-swollen by liquid[*]. We shall denote the volume fraction of elastomer by ϕ_2; the volume and side length before stretching are therefore $L_u^3\phi_2^{-1}$ and $L_u\phi_2^{-1/3}$, respectively. The elongation ratio relative to the swollen length is now[†] $\lambda = L\phi_2^{1/3}/L_u$ and the dilation on stretching $\Delta V = V - L_u^3\phi_2^{-1}$. Our aim, in the following section, will be to derive expressions for the dilation coefficient, which we define as $Y \equiv (\partial \ln V/\partial \lambda)_{P,T,\phi_2}$. The limiting value at $\lambda = 1$ will be denoted by Y_1.

(2) THEORIES OF THE VOLUME CHANGE

General equations

We begin by asking what general expressions can be found relating the dilation to the stretching force.

First among these we note:

$$\left[\frac{\partial V}{\partial L}\right]_{P,T} = \left[\frac{\partial f}{\partial P}\right]_{L,T} \tag{1}$$

and this is true for any elastic body. There is also good experimental evidence that, within the range we shall review, the bulk compressibility $\kappa \equiv -(\partial \ln V/\partial P)_T$ is unchanged by elongation, at least to a good

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[*] There are two ways of dealing with swollen materials. A complete theory represents the stored energy as a function simply of the principal strains, whether these arise from mechanical stresses or from swelling. The alternative is to treat a swollen sample as a different material. The definition of reduced force, which we shall wish to use, is based on the first alternative and we therefore choose this for our analysis. The results are then very simply convertible to those arising from the second alternative.

[†] Some authors use a separate symbol α for this quantity, but this seems unnecessary, so long as it is understood that λ is in all cases the extension ratio associated with the stretching process only.

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approximation[4]. By virtue of this, equation (1) can be supplemented by

$$Y = -\kappa L_u \phi_2^{-1/3} \left[\frac{\partial f}{\partial V}\right]_{L,T} \tag{2}$$

Next we recall that classical elasticity theory shows that for any isotropic body, in the limit of $\lambda = 1$,

$$Y_1 = \frac{\kappa \phi_2^{2/3}}{3L_u^2}\left[\frac{\partial f}{\partial \lambda}\right]_{P,T,\lambda=1} \tag{3}$$

All theoretical expressions, and all valid experimental data, must extrapolate to this limit.

To solve equation (2) generally we need expressions for f as a function of V and L, and in the following sections we consider in turn a number of possibilities[*].

The statistical theory

It is well established that the observed elasticity is a property of the molecular network. The simplest statistical theory[7] gives an expression for the increase in free energy Φ in any type of deformation, defined by the principal extension ratios λ_1, λ_2 and λ_3:

$$\Phi = CL_u^3(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{4}$$

where $C = \frac{1}{2}\nu kT\frac{\langle r^2\rangle_0}{\langle r^2\rangle_f}$ and $\langle r^2\rangle_0$ and $\langle r^2\rangle_f$ are respectively the mean square end-to-end distance in the undeformed network and in the free chain, ν is the number of chains in unit volume of the network at T and P, and k is Boltzmann's constant[†]. For simple elongation with or without pre-swelling, the principal extension ratios are $\lambda_1 = L/L_u$ and $\lambda_2^2 = \lambda_3^2 = VL^{-1}L_u^{-2}$; equation (4) then becomes:

$$\Phi = CL_u\left(L^2 + \frac{2V}{L} - 3L_u^2\right) \tag{5}$$

It is important to note that this equation holds for swollen samples as well as for unswollen, since we are concerned with the *total* deformation of the network, by swelling as well as by application of the stretching force. Hence we find, in either case:

$$f = \left[\frac{\partial \Phi}{\partial L}\right]_V = 2CL_u\left[L - \frac{V}{L^2}\right] \tag{6}$$

This is indistinguishable for most purposes from

$$f = 2CL_u^2\phi_2^{-1/3}(\lambda - \lambda^{-2}) \tag{7}$$

Returning to (6) we differentiate with respect to V, giving

$$(\partial f/\partial V)_L = -2CL_uL^{-2} \tag{8}$$

which in combination with equation (2) yields

$$Y = 2\kappa CL_u^2L^{-2}\phi_2^{-1/3} = 2\kappa C\phi_2^{1/3}\lambda^{-2} \tag{9}$$

Equation (7) is conveniently related to experimental measurements by defining a 'reduced force':

$$[f] = f\phi_2^{1/3}L_u^{-2}(\lambda - \lambda^{-2})^{-1} \tag{10}$$

In analogous fashion we now define a 'reduced dilation coefficient':

$$[D] = \lambda^2 Y\phi_2^{-1/3}\kappa^{-1} \tag{11}$$

For elastomers which obey the statistical theory we note that

$$[f] = [D] = 2C \tag{12}$$

A general framework

Viewed only as a method of interpreting experimental data, equation (4) is the simplest member of a general family of stored energy functions which represent Φ as the sum of independent contributions from the three principal strains. The general form can be written

$$\Phi = L_u^3(w_1 + w_2 + w_3) \tag{13}$$

where w_i represents the value of a function w when the principal strain is λ_i. (Thus in equation (4) $w_1 = c(\lambda_1^2 - 1)$.) It is convenient to use as variable $x_i \equiv \lambda_i^2$ and to define $\dot{w}_i \equiv \partial w/\partial x$ at $x = x_i$ and $\ddot{w}_i \equiv \partial^2 w/\partial x^2$ at $x = x_i$. Following the procedure used in the preceding section we obtain the results:

$$[f] = 2(\lambda\dot{w}_1 - \lambda^{-2}\dot{w}_2)(\lambda - \lambda^{-2})^{-1} \tag{14}$$

$$[D] = 2(\dot{w}_2 + \lambda^{-1}\phi_2^{-2/3}\ddot{w}_2) \tag{15}$$

Given an algebraic form for w these equations lead at once to expressions for the reduced force and reduced dilation coefficient. In the following sections we consider in turn a number of theoretical and empirical forms for w. It is of interest to observe the absence of w_1 from equation (15) and to recall that Treloar[3] pointed out that dilation arises from deformations at right angles to the direction of elongation, and that in consequence the stored energy function chosen must be able to describe general deformations.

w as a power series in x

Most of the empirical stored energy functions which have been proposed are based on the use of a series of terms of the form $w = \Sigma C_i(\lambda^{\alpha_i} - 1)$. To preserve this formulation we shall use

$$w = \Sigma C_i(x^{\frac{1}{2}\alpha_i} - 1) \tag{16}$$

Then $\dot{w} = \frac{1}{2}\Sigma\alpha_iC_ix^{(\frac{1}{2}\alpha_i - 1)}$ and $\ddot{w} = \frac{1}{2}\Sigma\alpha_i(\alpha_{i/2} - 1)C_ix^{(\frac{1}{2}\alpha_i - 2)}$. Putting $x_1 = \lambda^2\phi_2^{-2/3}$ and $x_2 = \lambda^{-1}\phi_2^{-2/3}$ we obtain from equations (14) and (15):

$$[f] = (\lambda^2 - \lambda^{-1})^{-1}\Sigma\alpha_iC_i\phi_2^{(2-\alpha_i)/3}(\lambda^{\alpha_i} - \lambda^{-\frac{1}{2}\alpha_i}) \tag{17}$$

$$[D] = \tfrac{1}{2}\Sigma\alpha_i^2C_i\phi_2^{(2-\alpha_i)/3}\lambda^{(1-\frac{1}{2}\alpha_i)} \tag{18}$$

We check that with $\alpha_i = 2$ these equations reduce to equation (12). In part 1[8] it was found convenient to express $[f]$ in the form

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[*] Other workers have discussed dilation from different points of view. See e.g. Chadwick[5], Odgen[6], Price[2] and Treloar[3].

[†] Some authors modify this stored energy function by introducing a numerical factor and/or by adding a term in $\ln(\lambda_1\lambda_2\lambda_3)$. Neither of these changes is significant in the present context.

$$[f]=\Sigma g_i F_i \tag{19}$$

where

$$F_i \equiv 2\alpha_i^{-1}(\lambda^{\alpha_i}-\lambda^{-\frac{1}{2}\alpha_i})(\lambda^2-\lambda^{-1})^{-1} \tag{20}$$

which tends to 1 as $\lambda \rightarrow 1$. Comparing this with equation (17) gives

$$g_i=\tfrac{1}{2}\alpha^2 c_i \phi_2^{(2-\alpha_i)/3} \tag{21}$$

In the same way we now define

$$D_i \equiv \lambda^{(1-\alpha_i/2)} \tag{22}$$

giving

$$[D]=\Sigma g_i D_i \tag{23}$$

In part 1[8] equation (19) was used as the basis for examining the problem of finding a stored energy function capable of expressing the observed elastic properties of a network over the widest possible range of deformation (not confined to simple elongation), and a minimum of three terms was found necessary. The data to be interpreted in this paper all arise from elongations within the approximate range $1<\lambda<2$. It seems appropriate therefore to lay down the ground rule that no equation to be evaluated should involve more than two arbitrarily adjustable parameters. On this basis we examine three equations based on power terms:

The Mooney equation. This 2-term equation for w specifies $\alpha_i=2$ and -2; the adjustable parameters are moduli, usually expressed as c_1 and c_2. In our formulation

$$w=c_1(x-1)+c_2(x^{-1}-1) \tag{24}$$

leading straightforwardly to

$$[f]=g_2+g_{-2}\lambda^{-1} \tag{25}$$

$$[D]=g_2+g_{-2}\lambda^2 \tag{26}$$

where

$$g_2=2c_1,\ g_{-2}=2c_2\phi_2^{4/3} \tag{27}$$

Alternative equation from part 1. The 3-term expression developed in part 1[8] specifies $\alpha_i=2$, 0 and 4. Of these we now neglect $\alpha_i=4$, which becomes important only at large deformation, leaving us again with two moduli to be assigned. Equation (20) becomes indeterminate at $\alpha_i=0$ and must be replaced by

$$F_0=3(\lambda^2-\lambda^{-1})^{-1}\ln\lambda \tag{28}$$

We then obtain

$$[f]=g_2+3g_0(\lambda^2-\lambda^{-1})^{-1}\ln\lambda \tag{29}$$

$$[D]=g_2+g_0\lambda \tag{30}$$

Treloar's general power series. Treloar[9] abandoned all prior specification of α_i and used a three term series, i.e. six parameters, but in the strain region of interest here 90% of the total force is represented by a single term with $\alpha_i \simeq 1.3$. For our present purpose we therefore use only one term, leaving α and g_α as the parameters to be adjusted:

$$[f]=2g_\alpha\alpha^{-1}(\lambda^\alpha-\lambda^{-\alpha/2})(\lambda^2-\lambda^{-1})^{-1} \tag{31}$$

$$[D]=g_\alpha\lambda^{(1-\alpha/2)} \tag{32}$$

Edward's theory of slipping links

Edwards[10] extended the statistical theory on the basis of an argument that the permanent crosslinks in a network will be supplemented by others, arising from entanglements, and subject to some degree of slip. His result is equivalent to

$$w=cL_u^3[x-1+v_s v^{-1}\{(x-1)(1+\eta x)^{-1} + \log(1+\eta x)-\log(1+\eta)\}] \tag{33}$$

where v and v_s are the numbers of permanent and slipping links, and η is a mean coefficient of slip, estimated as 0.2343 ($=\frac{1}{2}e^{-2}+1/6$). Using equations (14) and (15) we then find:

$$\tfrac{1}{2}[f]c^{-1}=1+v_s v^{-1}(\lambda^2-\lambda^{-1})^{-1}[\{1+\eta(2+\theta\lambda^2)\}(1+\theta\lambda^2)^{-2} - \lambda^{-3}\{1+\eta(2+\theta\lambda^{-1})(1+\theta\lambda^{-1})^{-2}\}] \tag{34}$$

$$\tfrac{1}{2}[D]c^{-1}=1+v_s v^{-1}(1+2\eta-\theta\lambda^{-1})(1+\theta\lambda^{-1})^{-3} \tag{35}$$

where $\theta=\eta\phi_2^{-2/3}$. These equations can be expressed in the forms

$$[f]=g_2+g_s F_s \quad \text{and} \quad [D]=g_2+g_s D_s \tag{36}$$

by introducing normalizing factors in F_s and D_s (with the reciprocal in g_s) of $(1+\theta)^3(1+2\eta-\theta)^{-1}$. By accepting the theoretical value of η we are thus left again with two adjustable parameters, g_2 and g_s.

Flory's theory of constraints

Flory's recent analysis[11] of network elasticity does not fall naturally into the same pattern, since he argues strongly against the identification of any specific entanglements and evaluates instead the overall constraints imposed by interaction of chains. To restrict ourselves to two parameters we examine only the original form of Flory's theory, in which the constraints are measured by a single parameter K and the reduced force can be expressed in the form

$$[f]=g_2[1+\psi_K(\lambda)] \tag{37}$$

where g_2 is the modulus calculated for a phantom network and ψ_K lies between 0 and 1. It is not conveniently expressible in explicit form but is readily evaluated from equation (14), using the set of equations derived by Flory. In the same way, from equation (15) we can evaluate X_K in the expression

$$[D]=g_2[1+X_K(\lambda)] \tag{38}$$

For an unswollen rubber, ψ_K and X_K can both be shown to become $K^2(K^2+1)(K+1)^{-4}$ at $\lambda=1$.

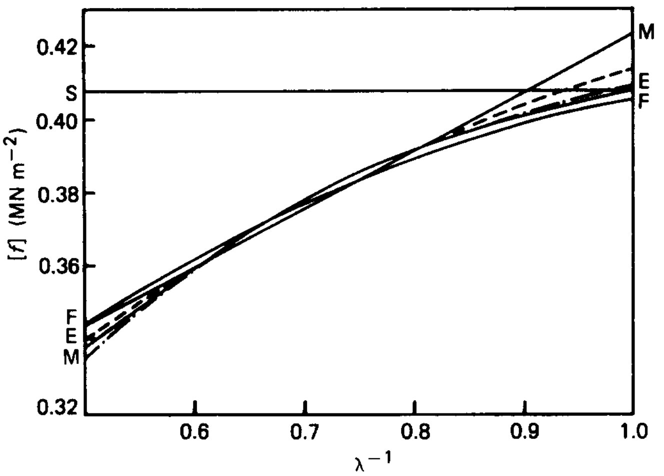

Figure 1 $[f]$ vs. λ^{-1} from various theories: solid lines: E = Edwards, F = Flory, M = Mooney, S = Statistical; broken lines: (– – –) Gee; (–·–·–) Treloar

Two unacceptable theories

Isotropic compressibilities. The earliest workers in the field suggested as a plausible hypothesis that the compressibility remains isotropic during elongation, i.e. that

$$(\partial \ln L/\partial P)_{f,T} = -\kappa/3 \qquad (39)$$

It was quickly pointed out[14,15] that this assumption is invalid, in that the linear compressibilities along and perpendicular to the direction of stretch are derivable from the stored energy function. In particular, the statistical theory requires, for the axial direction,

$$(\partial \ln L/\partial P)_{f,T} = -\kappa(\lambda^3+2)^{-1} \qquad (40)$$

Despite the fact that some agreement with experiment has been claimed for dilations calculated from equation (39) this approach must be discarded.

A hybrid of the statistical theory. What is probably the most widely used dilation equation is obtained[16] by eliminating c between equations (7) and (9) to give

$$Y = \kappa f \phi_2^{2/3} L_u^{-2}(\lambda^3-1)^{-1} \qquad (41)$$

This is equivalent to equating $[D]$ to the experimental value of $[f]$ which in practice is expressible by a Mooney equation, so that equation (41) leads to the result

$$[D] = g_2 + g_{-2}\lambda^{-1} \qquad (42)$$

There is no theoretical justification for this equation and as we shall see in sections (3) and (5) it is also inconsistent with experiment.

(3) COMPARISON WITH EXPERIMENT

In this section we examine the ability of the analyses developed above to fit the rather limited experimental evidence. The data to be used all derive from measurements of $(\partial f/\partial P)_{L,T}$. The general approach will be to use stress–strain data to assign values for the two parameters left adjustable in each analysis and from these to predict the dilation as a function of elongation.

Polybutadiene

Price and Allen[17] report dilation measurements for a crosslinked polybutadiene over the range of $0.90 > \lambda^{-1} > 0.565$, in which the reduced force is consistent with the Mooney equation (25) with $g_2 = 0.265$, $g_{-2} = 0.158$ giving $[f]_1 = 0.423$ MNm^{-2}. Using this equation to evaluate $[f]$ at $\lambda^{-1} = 0.8$ and 0.6 we then determine the parameters needed in other equations to reproduce these two values, with the following results:

Alternative equation (29) $g_2 = 0.232$, $g_0 = 0.181_5$, $[f]_1 = 0.413_5$
Treloar's equation (31) $\alpha = 1.37$, $g_\alpha = 0.409_5$, $[f]_1 = 0.409_5$
Edwards' equation (36) $g_2 = 0.261$, $g_s = 0.147$, $[f]_1 = 0.408$
Flory's analysis $K = 10$, $g_2 = 0.240$, $[f]_1 = 0.405_5$

The choice of $K = 10$ for Flory's analysis is somewhat arbitrary as it proved impossible to fit the two reference points exactly. The Mooney plots calculated using these parameters are plotted in *Figure 1*. All except the Mooney equation show appreciable curvature, as is inevitable in any equation capable of satisfactory representation of data near to and beyond $\lambda^{-1} = 1$ (see discussion in part 1[8]).

Using the parameters thus obtained, the reduced dilation coefficients can now be calculated, using equations (26), (30), (32), (36), (42) and Flory's analysis. In *Figure 2* the resulting curves are plotted, together with Price and Allen's experimental points, and some preliminary comments may be made:

(i) All acceptable analyses predict dilation greater than the statistical theory.

(ii) Edwards and Flory agree in predicting only a small increase.

(iii) Of the three empirical equations (26), (30) and (32), the alternative proposed in part 1 is marginally nearest to

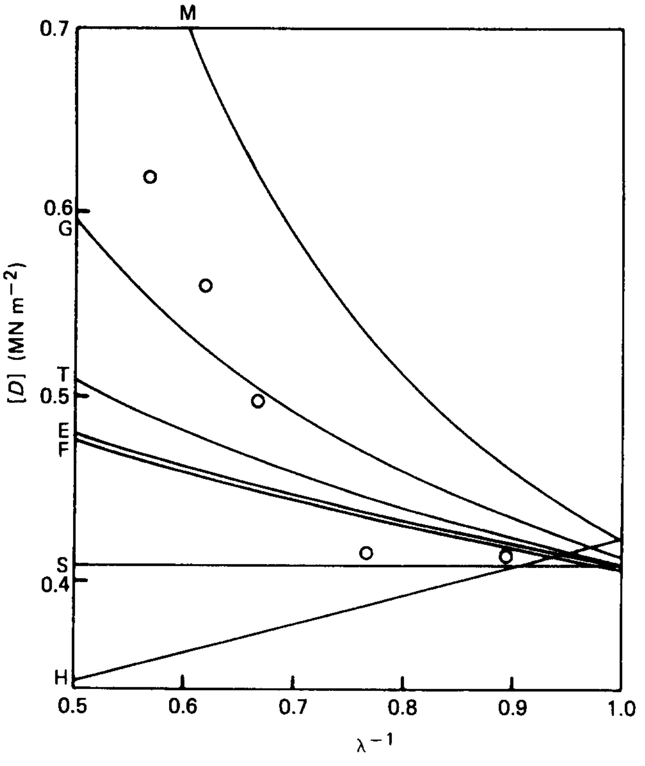

Figure 2 $[D]$ vs. λ^{-1} from various theories: lettering as in *Figure 1*, plus G = Gee, H = Hybrid, T = Treloar

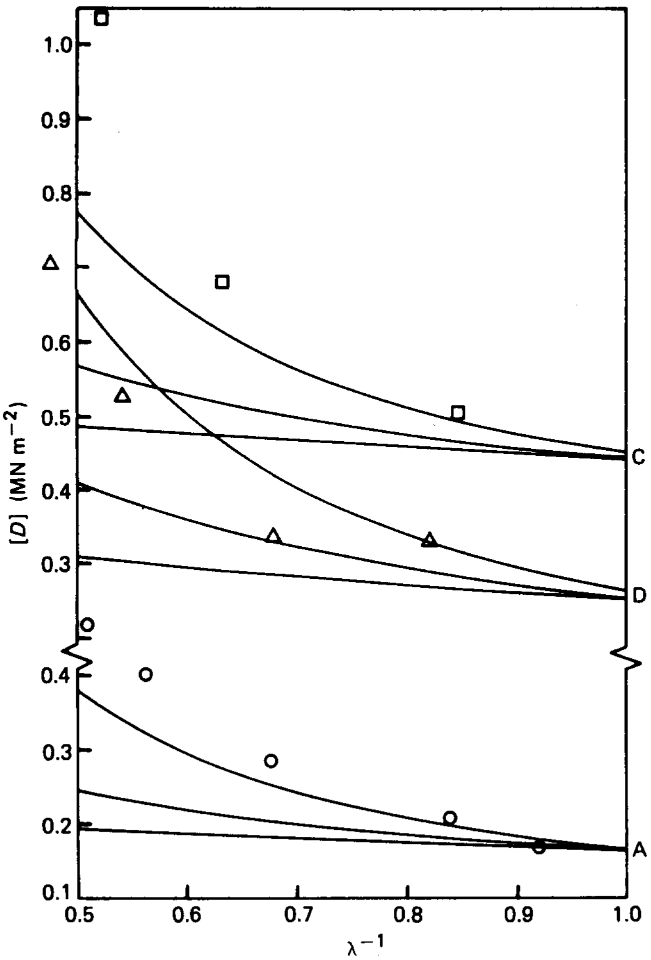

Figure 3 $[D]$ vs. λ^{-1} for natural rubbers C, D, A. 3 lines for each sample calculated from Mooney (top), Gee and Edwards (bottom)

experiment, but the form of strain dependence is not well reproduced.

(iv) The hybrid equation (42) discussed above predicts a dilation substantially less than the statistical theory.

Natural rubber

The most extensive series of measurements relate to five samples of natural rubber differing in degree of crosslinking[18]; the total of 22 measurements includes 5 in the swollen state. The samples cover a considerable range of c_1, c_2 and c_1/c_2 and all the data have been analysed as described above for polybutadiene. In *Figure 3* the results obtained are illustrated by plotting the data for three samples (unswollen) together with curves calculated from Mooney equations (25, 26), Gee equations (29, 30) and Edwards equation (36). Comparison with *Figure 2* shows that while the general pattern is the same, deviations from the statistical theory are appreciably larger than for polybutadiene. As already pointed out by Price[2], the Mooney equation now comes closest to a satisfactory fit. The data for swollen samples are too fragmentary to use in this sort of comparison, beyond noting with Price that they approach more closely to the predictions of the statistical theory.

(4) AN ADDITIONAL SOURCE OF DILATION?

The evidence briefly summarized above is interpreted to demonstrate a systematic departure from that predicted by any acceptable stored energy function we have examined (the Mooney equation has been clearly shown by Treloar[3] to be unacceptable). Within the very limited range of data, the departure from statistical theory is positive, is substantially reduced by swelling, and is dependent on the nature of the polymer. These observations suggest the existence of a source of dilation not due directly to the network stresses. It is now suggested that this may well arise from a packing problem produced by the rotational isomerization induced by elongation. Energy changes from this source are known to be important and it seems plausible to suppose that there could be an additional contribution to $(\partial V/\partial L)_{P,T}$ proportional to $f_e = (\partial V/\partial L)_{V,T}$ which has itself been shown to be proportional to f. We should then have

$$[D]_{\mathrm{exp}} - [D]_{\mathrm{calc}} = r(\lambda^3 - 1)[f] \qquad (43)$$

where $[D]_{\mathrm{calc}}$ derives from the network stresses as calculated above and r is a constant dependent on the volume change arising from isomerization. In *Figure 4* the data reviewed in section (3) are plotted in the form suggested by equation (43), using Edwards' equation for $[D]_{\mathrm{calc}}$. Looking first at the five natural rubber samples, it will be seen that points for any one rubber scatter satisfactorily about a line through the origin. Four of the five samples fit a single line, with $r = 0.21$. Sample A deviates notably and requires its own line $r = 0.32$. There is no ready explanation for this anomaly, but it would appear that any alternative analysis must encounter a similar difficulty in fitting A into the sequence. Points from polybutadiene scatter relatively more, as might be expected from the smallness of the correction; the line drawn gives $r = 0.08$.

Equation (43) has been deduced on the basis of a physical hypothesis for which we have no independent evidence*. Considered purely as a curve fitting device it is a significant improvement on any considered above, but of course it contains an additional parameter. A two parameter equation is obtainable from equation (43) by

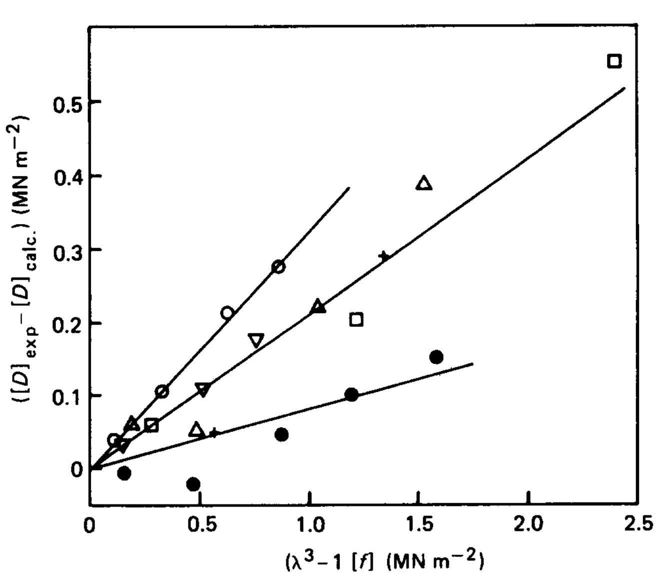

Figure 4 $[D]_{\mathrm{exp}} - [D]_{\mathrm{E}}$ vs. $(\lambda^3 - 1)[f]$: natural rubber samples A○, B+, C□, D△, E▽; polybutadiene ●

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* Bleha[19] has discussed the volume differences between rotamers.

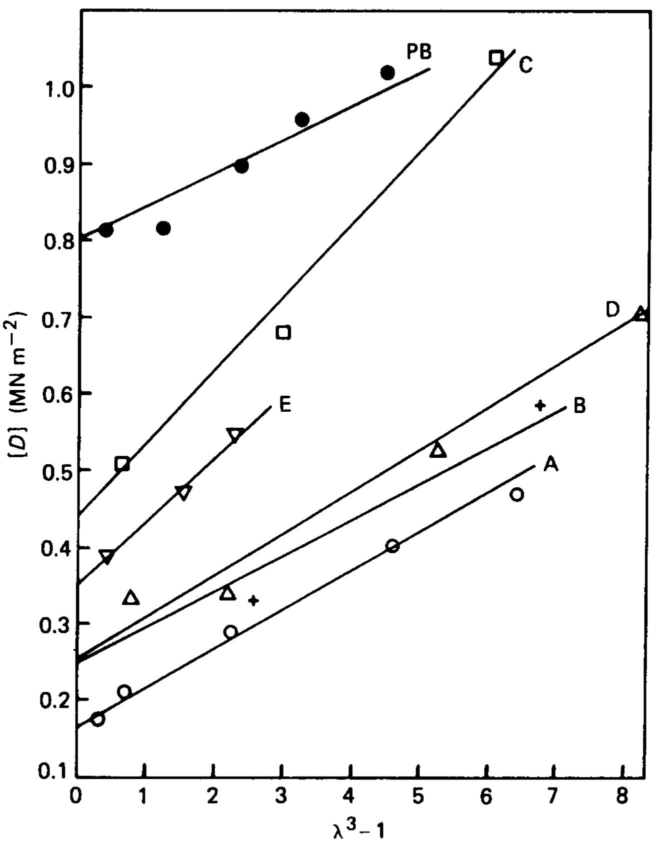

Figure 5 $[D]$ vs. (λ^3-1): points as in *Figure 4*. Subtract 0.4 from polybutadiene ordinates

Table 1 Constants $[f]_1$ and α^1 for 5 natural rubbers and polybutadiene

Rubber	$[f]_1$ (MNm^{-2})	α^1
Natural rubber A	0.163	0.31
B	0.249	0.20
C	0.440	0.22
D	0.251	0.22
E	0.350	0.24
Polybutadiene	0.405	0.10

replacing both $[D]_{\mathrm{calc}}$ and $[f]$ by the limiting value at $\lambda=1$, to give

$$[D]\simeq[f]_1\{1+r^1(\lambda^3-1)\} \tag{44}$$

where $[f]_1$ and r^1 are to be interpreted as empirical parameters. In *Figure 5* the data for polybutadiene and the five natural rubbers are plotted in the form of equation (44), choosing $[f]_1$, to conform to stress–strain data. The constants used are listed in *Table 1*. Our conclusion is that this is easily the most successful two-parameter empirical equation we have tested.

Data for swollen samples of natural rubber are too fragmentary to be capable of satisfactory analysis in this way. For the most part they show $[D]$ not differing widely from $[f]_1$ and the conclusion must be that dilation, like stress–strain behaviour, can reasonably be treated as nearly ideal in highly swollen samples. This is not inconsistent with the suggested effect of rotational isomerization, since the assumed packing problem is likely to be alleviated by the presence of the swelling agent.

(5) ENERGY CHANGES IN ELONGATION

We turn finally to consider the effect of dilation on the change of energy observed in elongation at constant pressure. Thermoelastic data have been widely used to evaluate $f_e/f \equiv f^{-1}(\partial V/\partial L)_{V,T}$ which is of importance as a measure of $T\partial\ln\langle r^2\rangle_0/\mathrm{d}t$. Most of the available data[20] derive from constant pressure measurements and therefore give $(\partial V/\partial L)_{P,T}$ from which f_e can be obtained using the relationship

$$f_e=\left[\frac{\partial U}{\partial L}\right]_{P,T}-\left[\frac{\partial U}{\partial V}\right]_{L,T}\left[\frac{\partial V}{\partial L}\right]_{P,T}$$

Taking for $(\partial U/\partial V)_{L,T}$ its bulk value $\beta T/\kappa$ where β is the coefficient of cubical expansion, we obtain:

$$\frac{f_e}{f}=\frac{1}{f}\left[\frac{\partial U}{\partial L}\right]_{P,T}-\frac{L_u^2\beta TY}{\kappa f} \tag{45}$$

The second term has been generally evaluated by using equation (41), whose derivation was criticized in section (2), yielding

$$\frac{f_e}{f}=\frac{1}{f}\left[\frac{\partial U}{\partial L}\right]_{P,T}-\frac{\beta T}{(\lambda^3-1)} \tag{46}$$

In the light of our study of dilation, equation (41) should be replaced by equation (44), which gives, in place of (46)

$$\frac{f_e}{f}=\frac{1}{f}\left[\frac{\partial U}{\partial L}\right]_{P,T}-\frac{\beta T}{(\lambda^3-1)}\frac{[f]_1}{[f]}\{1+r^1(\lambda^3-1)\} \tag{47}$$

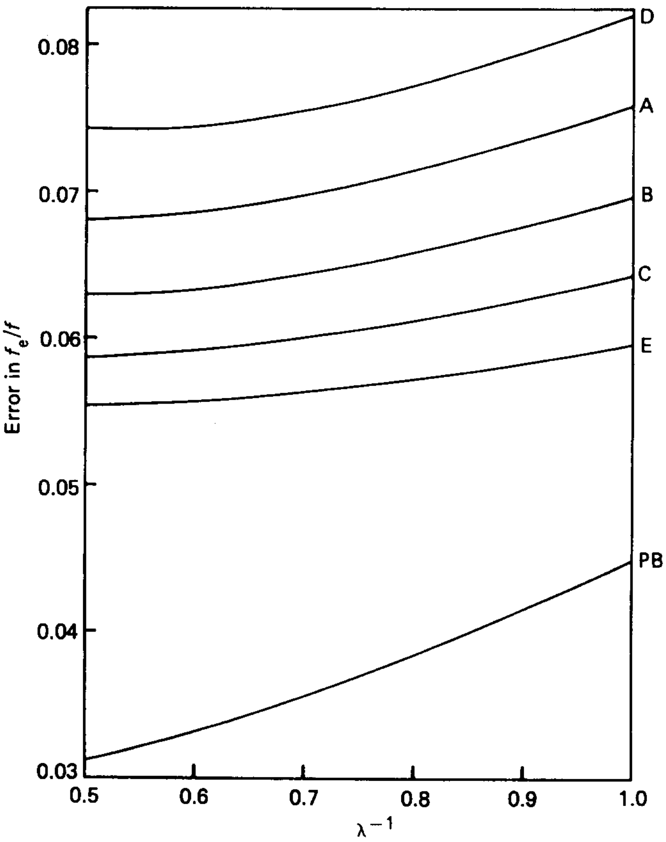

Figure 6 Error in f_e/f, from equations (47)–(46), taking $\beta T=0.2$

The significance of the proposed change has been examined by applying the two equations to the data on polybutadiene and natural rubber, calculating $[f]$ and $[f]_1$ from the Mooney constants assigned by the original investigators and taking $\alpha^1 = 0.10$ for polybutadiene, 0.24 for natural rubber. *Figure 6* shows the amount by which equation (46) overestimates f_e/f, taking equation (47) to be correct. The small dependence of the error on λ^{-1} shows that calculations based on equation (46) would show no internal evidence of error. We must nevertheless conclude that such calculations do involve systematic error which in the case of natural rubber amounts to an overestimate of f_e/f by *ca.* 0.06. Thus the mean value of 0.18 reported by Mark[20] should be revised downward to 0.12, bringing it into line with Price's direct measurements[2]. For polybutadiene the error is in the same sense, but only about half as large.

I gladly acknowledge helpful discussions with Dr C. Price. An earlier version of the paper was also discussed with Professor Treloar.

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