

Theoretical Stress/Temperature Relations for Rubber in Torsion

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The change of volume in a rubber cylinder subjected to combined axial extension and torsion is calculated. The result enables the formula for the couple, previously derived for an incompressible rubber, to be corrected for the effects of finite compressibility; for typical rubbers this correction is found to be negligible.

By thermodynamic analysis the temperature coefficient of the applied couple, under constant volume and constant pressure conditions, is derived. The difference between these two coefficients is related to the change of volume accompanying torsion at constant pressure.

THE thermodynamic analysis of the stress/temperature relations for rubber has in the past been almost exclusively concerned with simple extension. For this type of strain the accompanying volume changes give rise to an internal energy contribution to the stress which is relatively most important at low strains, where it leads to the phenomenon of the 'thermo-elastic inversion', i.e. the reversal of the slope of the stress/temperature curves at about eight per cent extension. As early as 1935, however, Meyer and Ferri¹ noted the effect of the thermal expansion of the material on its stress/temperature relations, and the absence of the inversion effect in uniaxial compression. Later, Meyer and van der Wyk² investigated the temperature dependence of shear stress in a coaxial-cylinder device, where volume change effects were expected to be non-existent, though, as pointed out by Flory, Ciferri and Hoeve³, this assumption is not strictly justified.

A type of strain which is closely related to simple shear is the torsion of a cylindrical rod. This type of strain has many experimental advantages; it is easy to produce, and the measurement of the torsional strain can be carried out with a relatively high degree of accuracy.

The purpose of the present paper is to examine the theoretical dependence of the torsional couple on temperature for a cylindrical rod which, for the sake of generality, will be considered to be subjected to combined axial extension and torsion about the axis. The analysis is based on the Gaussian network theory, and makes use of the relations between the changes of volume and the principal stresses derived in the preceding paper⁴.

In contrast to the case of simple extension, the problem of torsion involves an inhomogeneous state of strain, and is therefore rather more complicated. The following method of approach is adopted. First, the stress distribution is derived for the case of an incompressible rubber subjected to the specified strain. It is then assumed, initially, that this same stress distribution is applicable to a slightly compressible rubber; this enables the volume change at any point to be calculated. From this cal-

culated change in volume a correction to the initially assumed stress distribution is derived; this correction is found to be negligible. The resultant couple required to produce the torsion is thus approximately equal to that for an incompressible rubber.

From this result the stress/temperature relations are readily derived.

STRESS DISTRIBUTION IN CYLINDER SUBJECTED TO EXTENSION AND TORSION

The problem of the combined extension and torsion of a cylinder, for an incompressible rubber, has been dealt with by Rivlin⁴ using the most general type of stored-energy function. In this section the problem is worked out for the particular case of a stored-energy function derived from the statistical theory of the Gaussian network³; this is a special case of the more general solution given by Rivlin.

We consider a cylinder of unstrained radius a_0 subjected to an axial extension in the ratio β_3 , and a torsion about the axis of amount ψ , measured in radians per unit strained axial length. In the transverse plane normal to the cylinder axis the subscripts 1 and 2 will be used for the circumferential and radial directions, respectively; the circumferential and radial normal components of stress at any point are thus t_{11} and t_{22} . The element of the material at any radial position r is in a state of strain corresponding to a pure homogeneous strain together with a simple shear. The derivation of the stress components for such a state of strain is given in the Appendix. From this we obtain, for the radial stress component,

$$t_{22} = -p^* + (G'/V)\beta_2^2 \quad (1)$$

where β_2 is the radial extension ratio ($\beta_2 < 1$) referred to the unstrained dimensions, p^* has been defined³, and

$$G' = \nu kT (\bar{r}_1^2 / \bar{r}_0^2) \quad (2)$$

ν being the number of chains in the volume V under consideration. The quantity $\bar{r}_1^2 / \bar{r}_0^2$ is the ratio of the mean-square end-to-end chain length in the network to that for the uncrosslinked molecules. The quantity G'/V is equivalent to the modulus in simple shear. The shear strain γ at the radial position r is

$$\gamma = \psi r \quad (3)$$

The difference of radial and circumferential normal stress components is (see Appendix)[†]

$$t_{11} - t_{22} = (G'/V)(\beta_1^2 - \beta_2^2 + \beta_3^2 \psi^2 r^2) \quad (4)$$

For the equilibrium of stresses in the transverse plane it is easily shown that⁴

$$dt_{22}/dr = (t_{11} - t_{22})/r \quad (5)$$

[†]The symbols $\beta_1, \beta_2, \beta_3$ are used to distinguish these extension ratios from the principal extension ratios (axes of strain ellipsoid), which are denoted by λ_1, λ_2 , and λ_3 in ref. 3.

The above equations are applicable to both a compressible and an incompressible rubber (except that for an incompressible rubber, p^* in equation (1) is replaced by the arbitrary constant p). For an incompressible rubber we have

$$V = V_u; \quad \beta_1^2 = \beta_2^2 = \beta_3^{-1}; \quad r = r_0 \beta_3^{-1/2} \quad (6)$$

where V_u is the unstrained volume and r_0 the unstrained radial position. Insertion of these relations into equation (5) gives

$$\frac{dt_{22}}{dr} = (G'/V_u) \beta_3^2 \psi^2 r \quad (7)$$

This is the differential equation which determines the radial distribution of stress. Integration, subject to the boundary condition that $t_{22} = 0$ at the surface ($r = a_0 \beta_3^{-1/2}$), yields the result

$$t_{22} = - (G'/2V_u) \psi^2 \beta_3 (\alpha_0^2 - r_0^2) \quad (8)$$

which is equivalent to the expression given by Gent and Rivlin⁵.

Equation (8) represents a normal pressure (t_{22} negative) in the radial direction, which is a maximum at the axis and decreases parabolically with increasing r . It is proportional to the *square* of the torsion.

The couple M about the axis is derived from the tangential stress component t_{13} on the transverse section. [Appendix, equation 73(a)]. With (3) this becomes

$$t_{13} = (G'/V_u) \beta_3 \psi r / \beta_1 \beta_2 \quad (9)$$

The tangential force acting on an annulus of thickness dr being t_{13} ($2\pi r dr$), the contribution dM of the annulus to the total couple about the axis is

$$dM = 2\pi (G'/V_u) (\psi \beta_3 r^3 / \beta_1 \beta_2) dr \quad (10)$$

For an *incompressible* rubber the relations (6) apply, and $dr = \beta_3^{-1/2} dr_0$. Equation (10) then becomes

$$dM = 2\pi \psi (G'/V_u) r_0^3 dr_0 \quad (11)$$

giving the total couple

$$M = \int_0^{\alpha_0} dM = \frac{1}{2} \pi \psi (G'/V_u) \alpha_0^4 \quad (12)$$

which is independent of the axial extension β_3 .

VOLUME CHANGE FOR COMPRESSIBLE RUBBER

Since β_2 is a principal axis of the strain ellipsoid and t_{22} a principal stress, the volume-change relations previously derived³ are applicable, i.e.

$$t_{22} = (V - V_u) / KV + (G'/V) (\beta_2^2 - 1) \quad (13)$$

Putting $(V - V_u) = \delta V$ and inserting the expression (8) for t_{22} , the volume

change for a cylindrical shell of volume V at the radial position r is therefore given by

$$\frac{\delta V}{KV} = -\frac{G'}{2V_u} \psi^2 \beta_3 (\alpha_0^2 - r_0^2) - \frac{G'}{V} (\beta_3^2 - 1) \quad (14)$$

To the degree of approximation with which we are concerned we may put $V = V_u$ and $\beta_3^2 = \beta_3^{-1}$. Equation (14) may then be written

$$\delta V = KG' \left[-\frac{1}{2} \psi^2 \beta_3 (\alpha_0^2 - r_0^2) + (1 - 1/\beta_3) \right] \quad (14a)$$

To obtain the total volume change it is necessary to integrate (14a) with respect to r_0 . It must be noted, however, that G' , being proportional to the volume of the cylindrical shell, is a function of r_0 . We therefore write, for a cylinder of unit unstrained length,

$$G' = (G'/V_u) V_u = (G'/V_u) 2\pi r_0 dr_0 \quad (15)$$

where G'/V_u (the modulus) is now a constant. Inserting this expression into equation (14a), the total volume change is given by

$$\Delta V = \frac{KG'}{V_u} \int_0^{\alpha_0} \left[-\frac{1}{2} \psi^2 \beta_3 (\alpha_0^2 - r_0^2) + (1 - 1/\beta_3) \right] 2\pi r_0 dr_0 \quad (16)$$

On integration this yields

$$\Delta V = \pi \alpha_0^2 \frac{KG'}{V_u} \left[(1 - 1/\beta_3) - \frac{1}{4} \beta_3 \psi^2 \alpha_0^2 \right] \quad (17)$$

In this expression $\pi \alpha_0^2$ is the volume of the unstrained cylinder. If this is now represented by V_u , equation (17) becomes

$$(\Delta V/V_u) = (KG'/V_u) \left[(1 - 1/\beta_3) - \frac{1}{4} \beta_3 \psi^2 \alpha_0^2 \right] \quad (18)$$

Equation (18) represents the relative volume change for the whole cylinder. We shall also require the volume change for the material comprised within an initial radius r_0 . This is

$$[\Delta V]_{r_0}^{\alpha_0} = \frac{KG'}{V_u} \int_0^{r_0} \left[-\frac{1}{2} \psi^2 \beta_3 (\alpha_0^2 - r_0^2) + (1 - 1/\beta_3) \right] 2\pi r_0 dr_0$$

or

$$\left[\frac{\Delta V}{V_u} \right]_0^{r_0} = \frac{KG'}{V_u} \left[(1 - 1/\beta_3) - \frac{1}{4} \psi^2 \beta_3 (2\alpha_0^2 - r_0^2) \right] \quad (19)$$

where V_u now refers to the original volume within the radius r_0 .

It is seen that expression (18) for the change of volume for a cylinder subjected to combined extension and torsion is made up of two terms. The first term represents an increase of volume due to the extension; this has the form already derived³. The second term, representing the additional effect of the torsion, corresponds to a reduction of volume, and is proportional to the square of the torsion. This second term is directly related to the radial stress component t_{22} , which, as we have already seen, is compressive and also proportional to the square of the torsion.

It may be noted in passing that, for a particular relation between the extension and torsion, the volume change is zero. The appropriate condition, obtained by equating the RHS of equation (18) to zero, is that

$$\beta_3 = 1 \pm (1 - \psi^2 \alpha_0^2)^{1/2} / \frac{1}{2} \psi_0^2 \alpha_0^2 \quad (20)$$

which has a real solution only if $\psi_0^2 \alpha_0^2 \gg 1$.

EFFECT OF VOLUME CHANGE ON COUPLE

To obtain the effect of the volume change on the applied couple M , it is necessary first to derive the change in the state of strain at the radial position r . From this the change in the stress component t_{13} is obtained. Integration then gives the effect on the total couple.

It is assumed throughout that the axial extension ratio β_3 is constant. The circumferential and radial extension ratios β_1 and β_2 are given by

$$\beta_1 = r/r_0, \quad \beta_2 = dr/dr_0 \quad (21)$$

If β_{10} refers to the incompressible rubber, then

$$\beta_{10} = \beta_3^{-1/2} \quad (22)$$

and is independent of radial position. For a compressible rubber the change $\delta\beta_1$ in β_1 due to the compressibility is obtained from the change in volume ΔV for the material within the radius r_0 , as given by equation (19). Since $V = \pi\beta_3 r^2$

$$\delta\beta_1/\beta_{10} = \frac{\delta r}{r_0} = \frac{1}{2} [\Delta V/V_u]_{r_0} \quad (23)$$

The change in β_2 is not required for the present analysis. Its value may readily be obtained, if required, from the relation (for constant β_3)

$$\delta V/V_u = \delta\beta_1/\beta_{10} + \delta\beta_2/\beta_{20} \quad (24)$$

where $\delta V/V_u$ is the local volume change, given by equation (14a).

The contribution of a cylindrical shell to the total couple, represented by equation (10), when expressed in terms of the original radius r_0 through equations (21), becomes

$$dM = 2\pi\psi (G'/V_u) \beta_3 \beta_1^2 r_0^3 dr_0 \quad (25)$$

Writing

$$\beta_1^2 = \beta_{10}^2 (1 + 2\delta\beta_1/\beta_{10}) = \beta_3^{-1} (1 + 2\delta\beta_1/\beta_{10}) \quad (26)$$

[from equation (22)], the total couple is thus given by

$$M = 2\pi\psi (G'/V_u) \int_0^{a_0} (1 + 2\delta\beta_1/\beta_{10}) r_0^3 dr_0 \quad (27)$$

This can be written in the form

$$M = M_0 + \delta M \quad (27a)$$

where M_0 is the couple for the incompressible rubber, given by equation (12), and

$$\delta M = 2\pi\psi (G'/V_u) \int_0^{a_0} 2 (\delta\beta_1/\beta_{10}) r_0^3 dr_0 \quad (28)$$

The relative change in M due to the compressibility is $\delta M/M_0$. Using the expression (10) for M_0 this becomes

$$\frac{\delta M}{M_0} = \frac{4}{a_0^4} \int_0^{a_0} 2 (\delta\beta_1/\beta_{10}) r_0^3 dr_0 \quad (29)$$

On insertion of expression (23), together with (19), for $\delta\beta_1/\beta_{10}$, we thus obtain

$$\frac{\delta M}{M_0} = \frac{4}{a_0^4} \frac{KG'}{V_u} \int_0^{a_0} [(1 - 1/\beta_3) - \frac{1}{2}\psi^2\beta_3 (2a_0^2 - r_0^2)] r_0^3 dr_0 \quad (30)$$

which yields

$$\delta M/M_0 = (KG'/V_u) [(1 - 1/\beta_3) - \frac{1}{3}\beta_3\psi^2 a_0^2] \quad (31)$$

This equation represents the effect of the compressibility on the magnitude of the couple, for given values of the unstrained radius a_0 , and of the strain parameters β_3 and ψ . It is seen that this expression has a form comparable to that for the volume change itself [equation (18)], being composed of two terms, one related to the extension and the other to the torsion.

MAGNITUDE OF VOLUME-CHANGE EFFECTS

The value of the compressibility coefficient K for rubber is approximately $5 \times 10^{-5} \text{ cm}^2 \text{ kg}^{-1}$ while a typical value for G'/V_u (shear modulus) is 4 kg cm^{-2} . Hence G'/V_u is of the order 10^{-4} . In a torsional experiment the maximum value of ψa_0 is likely to be of the order unity. Thus from equation (18) it is seen that the maximum value of the relative volume change in torsion is of the same order (though of opposite sign) to that for simple extension, i.e. of the order 10^{-4} . In combined extension and torsion the volume change can range from zero to this same maximum, depending on the relative amounts of extension and torsion.

The relative change in couple due to this change of volume [equation (31)] is of the same order as the volume change itself, i.e. *ca.* 10^{-4} . (A similar relationship applies to all the components of stress.) The correction to the value of the couple when the volume change is taken into account is therefore negligible.

STRESS / TEMPERATURE RELATIONS

In this section the temperature coefficients of the torsional couple at constant pressure and at constant volume are considered. The derivation is formally similar to that of Flory, Ciferri and Hoeve⁶ for simple extension.

In deriving these temperature coefficients the correction to the couple due to compressibility, represented by equation (31), will be ignored. This is justified by the negligible value of this correction, and by the fact that so long as K is no more strongly dependent on temperature than is G' (which seems entirely reasonable) the *relative* temperature variation of $\delta M/M_0$ will be of the same order as that of M_0 itself, and will therefore be equally negligible. This means that we use the relation (12), which is strictly valid only for an incompressible rubber, to represent the couple in the case of the compressible rubber also. Insertion of expression (2) for G' in (12) gives

$$M = \frac{1}{2} \pi \psi (v k T / V_u) (\bar{r}_i^2 / \bar{r}_0^2) a_0^4 \quad (32)$$

Constant pressure

It is required to differentiate equation (32) at constant pressure p , length l and torsion ψ . In this expression, V_u (unstrained volume), a_0 (unstrained radius), \bar{r}_i^2 and \bar{r}_0^2 are functions of temperature. Writing

$$(1/V_u) \partial V_u / \partial T = \partial \ln V_u / \partial T = \beta \quad (33a)$$

where β is the volume expansion coefficient of the unstrained rubber, we have

$$\partial \ln V_u^{-1} / \partial T = -\beta \quad (33b)$$

and

$$\partial \ln a_0^4 / \partial T = 4\beta / 3 \quad (33c)$$

Also, since \bar{r}_i^2 , the mean-square chain end-to-end distance in the unstrained state, is proportional to $V_u^{2/3}$

$$d \ln \bar{r}_i^2 / dT = 2\beta / 3 \quad (34)$$

Remembering that if $f(x) = u \cdot v \cdot w \dots$, where $u, v, w \dots$ are functions of x , then

$$\left[\frac{\partial \ln f(x)}{\partial x} \right]_u = \frac{\partial \ln v}{\partial x} + \frac{\partial \ln w}{\partial x} + \dots \quad (35)$$

the differential of equation (32) is seen to be

$$\left[\frac{\partial \ln (M/T)}{\partial T} \right]_{p,l,\psi} = -\beta + \frac{2\beta}{3} - \frac{d \ln \bar{r}_0^2}{dT} + \frac{4\beta}{3}$$

or

$$\left[\frac{\partial \ln (M/T)}{\partial T} \right]_{p,l,\psi} = \beta - \frac{d \ln \bar{r}_0^2}{dT} \quad (36)$$

This may be written

$$\left(\frac{\partial M}{\partial T} \right)_{p,l,\psi} = \frac{M}{T} \left[1 + \beta T - T \frac{d \ln \bar{r}_0^2}{dT} \right] \quad (36a)$$

Constant volume

Strictly, the expression for the couple should be differentiated at constant final volume $V_u - \Delta V$, where ΔV is given by equation (18). However, by the same arguments which were used to justify ignoring δM , we may justifiably ignore ΔV in deriving the temperature coefficient of M , since the change ΔV makes a negligible difference to M . Differentiation at constant V (i.e. V_u) then gives

$$\left[\frac{\partial \ln(M/T)}{\partial T} \right]_{V, l, \psi} = - \frac{d \ln \bar{r}_0^2}{dT} \quad (37)$$

or

$$\left(\frac{\partial M}{\partial T} \right)_{V, l, \psi} = \frac{M}{T} \left[1 - T \frac{d \ln \bar{r}_0^2}{dT} \right] \quad (37a)$$

Difference between temperature coefficients

The difference between the temperature coefficients at constant pressure and at constant volume respectively, is

$$\left[\frac{\partial \ln(M/T)}{\partial T} \right]_{P, l, \psi} - \left[\frac{\partial \ln(M/T)}{\partial T} \right]_{V, l, \psi} = \beta \quad (38)$$

Comparison with Flory

The result represented by equation (37) is a special case of the general result enunciated by Flory⁷, that for any type of distortion the logarithmic temperature coefficient of the stress is equal to $-d \ln \bar{r}_0^2/dT$. Furthermore, the fact that the temperature coefficients at constant pressure and at constant volume are not equal substantiates and amplifies the conclusion arrived at by Flory, Ciferri and Hoeve⁸ on general grounds, namely that the apparent absence of a volume change in torsion, as indicated by the classical theory of elasticity for small strains, does not justify the assumption that for this type of strain the stress/temperature coefficients at constant pressure and at constant volume are identical.

RELATION OF INTERNAL ENERGY TO CHANGE OF VOLUME

For simple extension the internal energy contribution f_e to the stress, at constant volume, is obtained from the relation,

$$f = \left(\frac{\partial E}{\partial l} \right)_{V, T} + T \left(\frac{\partial f}{\partial T} \right)_{V, l} = f_e + T \left(\frac{\partial f}{\partial T} \right)_{V, l} \quad (39)$$

The analysis of Flory, Ciferri and Hoeve⁸ then yields

$$f_e/f = -T \left[\partial \ln(f/T) / \partial T \right]_{V, l} = T d \ln \bar{r}_0^2 / dT \quad (39a)$$

The same type of analysis is applicable to torsion, on substituting M

for f and ϕ , the angular rotation, for l . Let us denote by M_{ev} the internal energy contribution to the couple at constant volume. Then

$$M_{ev} = \left(\frac{\partial E}{\partial \phi} \right)_{T, V, l} = M - T \left(\frac{\partial M}{\partial T} \right)_{V, \phi, l} = M - T \left(\frac{\partial M}{\partial T} \right)_{V, \psi, l} \quad (40)$$

and

$$M_{ev}/M = -T [\partial \ln (M/T) / \partial T]_{V, \psi, l} = T d \ln \bar{r}_0^2 / dT \quad (41)$$

A similar analysis gives the change in heat content in a constant pressure experiment. Neglecting the contribution $p dV$ (where p denotes atmospheric pressure) it is essentially the internal energy contribution to the stress at constant pressure. Denoting this by M_{ep} ,

$$M_{ep}/M = -T [\partial \ln (M/T) / \partial T]_{p, l, \psi} = T [d \ln \bar{r}_0^2 / dT - \beta] \quad (42)$$

The difference between the internal energy contributions to the stress at constant pressure and at constant volume, respectively, is thus

$$M_{ep} - M_{ev} = -M\beta T \quad (43)$$

It will now be shown that this difference is exactly equal to the change in internal energy associated with the change of volume due to the torsion. From equation (18) the total change of volume (on stretching and twisting) is

$$\Delta V = KG' [(1 - 1/\beta_3) - \frac{1}{2}\beta_3\psi^2\alpha_0^2] \quad (44)$$

The change of volume per unit increase of torsion is thus

$$(dV/d\psi)_{T, p, l} = -\frac{1}{2}KG' \beta_3 \psi \alpha_0^2 \quad (45)$$

The internal energy change associated with a change of volume dV in a liquid, as quoted by Gee⁸, is†

$$(dE/dV)_T = \beta T / K \quad (46)$$

Hence

$$\left(\frac{\partial E}{\partial \psi} \right)_{T, p, l} - \left(\frac{\partial E}{\partial \psi} \right)_{T, V, l} = \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial \psi} \right)_{T, p, l} = -\frac{1}{2}\beta TG' \beta_3 \psi \alpha_0^2 \quad (47)$$

Combining equations (47) and (12)

$$\left(\frac{\partial E}{\partial \psi} \right)_{T, p, l} - \left(\frac{\partial E}{\partial \psi} \right)_{T, V, l} = -M\beta T \frac{\beta_3 V_u}{\pi \alpha_0^2} \quad (48)$$

But $V_u = \pi \alpha_0^2 l / \beta_3$, and therefore

$$\left(\frac{\partial E}{\partial \psi} \right)_{T, p, l} - \left(\frac{\partial E}{\partial \psi} \right)_{T, V, l} = -M\beta T l \quad (49)$$

In terms of the angle of rotation ϕ , where $d\phi = l d\psi$, this becomes

$$\left(\frac{\partial E}{\partial \phi} \right)_{T, p, l} - \left(\frac{\partial E}{\partial \phi} \right)_{T, V, l} = -M\beta T \quad (50)$$

†In Gee's paper, β is the linear expansion coefficient.

Comparison with equation (43) shows the right-hand sides of these two equations to be identical. Thus the difference between the internal energy changes at constant volume and at constant pressure is directly associated with the change of volume in the latter case.

It is interesting to note that the effect of the volume change on the internal energy is significant, even though this volume change is proportional to the square (not the first power) of the torsion, and even though the direct effect of the change of volume on the torsional couple is negligible.

THERMO-ELASTIC INVERSION

For simple extension we have⁶, for an extension ratio α

$$[\partial \ln (f/T) / \partial T]_{p,l} = -d \ln \bar{r}_0^2 / dT - \beta / (\alpha^3 - 1) \quad (51)$$

which can be transformed to

$$\left(\frac{\partial f}{\partial T} \right)_{p,l} = \frac{f}{T} \left[1 - T \frac{d \ln \bar{r}_0^2}{dT} - \frac{\beta T}{\alpha^3 - 1} \right] \quad (51a)$$

The inversion point is given by the value of σ at which $(\partial f / \partial T)_{p,l} = 0$, i.e. by the equation

$$\beta T / (\alpha^3 - 1) = 1 - T d \ln \bar{r}_0^2 / dT \quad (52)$$

For natural rubber, the experiments of Allen, Bianchi and Price⁹ give

$$d \ln \bar{r}_0^2 / dT \approx 0.2 (1/T) \quad (53)$$

so that equation (52) has a solution at a positive value of $\alpha^3 - 1$.

The comparable relation for torsion [equation (36a)] is

$$\left(\frac{\partial M}{\partial T} \right)_{p,l,\psi} = \frac{M}{T} \left[1 + \beta T - T \frac{d \ln \bar{r}_0^2}{dT} \right] \quad (54)$$

Since this does not contain ψ , the stress/temperature coefficient has the same sign for all values of the torsion, i.e. there can be no thermoelastic inversion.

DIAGRAMMATIC REPRESENTATION

Typical examples of the dependence of the couple on temperature, under constant pressure conditions, are shown diagrammatically in *Figure 1*, (the range of temperature being sufficiently small for linearity to be assumed). For natural rubber, $\beta = 6.6 \times 10^{-4}$; hence at $T = 300^\circ\text{K}$, $\beta T = 0.20$. If $d \ln \bar{r}_0^2 / dT = 0$, the resultant slope is represented by the line AC. If, however, we insert $T d \ln \bar{r}_0^2 / dT = 0.2$ from the experimental result (53) for natural rubber, then M is approximately proportional to T (line AB).

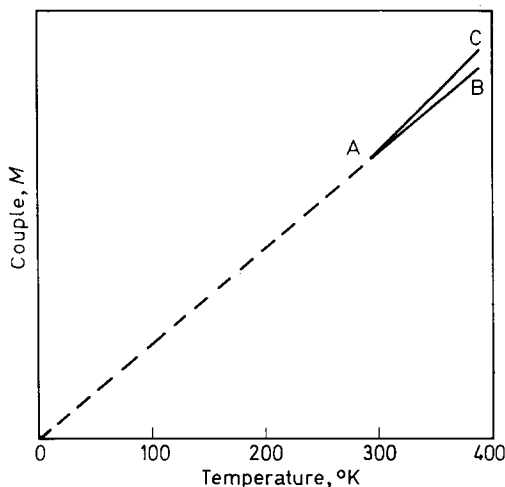


Figure 1—Relation between couple and temperature at constant pressure [equation (36a)]

$$AC \quad \beta T = 0.20, T d \ln \bar{r}_0^2 / dT = 0$$

$$AB \quad \beta T = 0.20, T d \ln \bar{r}_0^2 / dT = 0.20$$

The form of the curves in *Figure 1* is independent of the amount of the torsion ψ . This affects only the vertical scale factor.

DISCUSSION

The equations for the stress/temperature coefficient at constant volume (37, 37a) are formally identical to those for simple extension, with the substitution of M and ψ for f and l . The differences between the stress/temperature coefficients at constant pressure and at constant volume, however, are not of the same form, the term β in equation (38) being replaced by $-\beta/(\alpha^3-1)$ in the corresponding equation for simple extension (α being the extension ratio). The effect of this is most significant at small strains, since when $\alpha \rightarrow 1$ the quantity $-\beta/(\alpha^3-1)$ tends to infinity. Correspondingly, the quantity $(\partial E/\partial l)_{p,T}$ for simple extension remains finite as $f \rightarrow 0$, while for torsion M_{cp} or $(\partial E/\partial \phi)_{p,T,1}$ is proportional to M [equation (42)] and hence vanishes when $M=0$. These differences reflect the different form of dependence of the volume change on the strain in the two cases; for a tensile strain the volume change is approximately proportional to the strain, while for torsion it is proportional to the square of the strain. As a result, the effects of the volume change are much less apparent in the case of small torsional strains than in the case of small tensile strains.

It has been shown that a direct relation exists between the differences of internal energy changes as derived from the temperature coefficients of M at constant pressure and at constant volume, and the change of volume due to the torsion, at constant pressure. At first sight this result seems surprising, since the calculated values of the couple were obtained by

ignoring the effect of the volume change. The explanation of this apparent inconsistency is that while both $(\partial V/\partial\psi)_{T,p,l}$ and $(dE/dV)_T$ contain the compressibility K , the product of these two quantities, which represents the contribution of the volume change to the internal energy change associated with the torsion, does not. (The same applies to $(\partial E/\partial l)_{T,p} - (\partial E/\partial l)_{T,v}$ in simple extension, as can be seen from equations (12) and (14) of Gee's paper³, in which it was assumed that $(\partial E/\partial l)_{T,v}$ was zero.) Hence the change of internal energy which arises from compressibility effects is *independent* of the numerical value of the compressibility (provided that this is small compared with $1/G'$). Looking at the problem in this way we can see that the results would be unchanged if, in place of the actual value of compressibility, we were to substitute an indefinitely small, but non-zero value. The quantity δM , representing the difference in the couple arising from the change of volume, could then be made indefinitely small. Thus in the limit, as $K \rightarrow 0$, $M \rightarrow M_0$, and the equations for the couple, and its temperature coefficients, instead of being approximations, become exact. The treatment given is therefore an exact treatment for the case when the compressibility is indefinitely small; it remains a very close approximation in the case when $KG' \approx 10^{-4}$.

It is desirable to reiterate the restrictions implied by the use of the Gaussian network model in the interpretation of stress/temperature relations. As stated in the preceding paper³, this model divides the free energy of deformation into two entirely separate terms, one associated with the change of volume, which is independent of strain, and the other related to the deformation of the network. On this basis, any changes of internal energy measured under *constant volume* conditions must be interpreted as arising from the dependence of internal energy on the mean square chain vector length. It should, however, be borne in mind that while such a dependence of internal energy on chain dimensions must give rise to a term of the type postulated, this is not necessarily the *only* factor which could possibly be involved. It is not necessarily true that the internal energy associated with the *inter*-molecular force fields is a function of volume only; it is possible—and at high degrees of orientation probable—that the state of local orientation may also be a factor in the situation, giving a contribution to the intermolecular internal energy even at constant volume. Hence equations of the type (37) or (40) do not represent *thermodynamic* necessities; they are valid only in so far as the physical model on which they are based is valid.

APPENDIX

Pure homogeneous strain plus simple shear

Helmholtz free energy—Consider a unit cube with edges OA, OB, OC, parallel to coordinate axes OX, OY, OZ. This is subjected to a pure homogeneous strain whereby the edge lengths become β_1 , β_2 and β_3 , respectively. Thus the face normal to OY changes from the square OBDA (Figure 2) to the rectangle OB'D'A', where OA' = β_1 and OB' = β_3 . Application of an additional shear strain parallel to OX converts this to the parallelogram OB''D''A', the y dimension (β_2) remaining unchanged. The

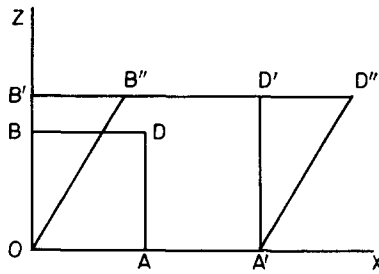


Figure 2

shear strain, referred to the dimensions in the state of pure homogeneous strain, is

$$\gamma = B'B'' / OB' \quad (55)$$

It is required to determine $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$ for the final strained state, where λ_1 , λ_2 and λ_3 are the principal axes of the strain ellipsoid. This can be done without actually deriving the principal axes, by making use of the result that the sum of the squares of any three mutually perpendicular lines of unit length, when subjected to a pure homogeneous strain, is independent of the directions of the axes of strain, and equal to the sum of the squares of the principal axes of the strain ellipsoid[†]. In the present case

$$OA'^2 + OC'^2 + OB''^2 = \beta_1^2 + \beta_2^2 + \beta_3^2 (1 + \gamma^2) \quad (56)$$

The expression for the free energy is therefore

$$A = A^* + \frac{1}{2}G' [\beta_1^2 + \beta_2^2 + \beta_3^2 (1 + \gamma^2)] \quad (57)$$

Components of stress

To find the components of stress, we consider a specimen whose surfaces in the final state are normal to OX, OY and OZ, forming a rectangular parallelepiped of dimensions β_1 , β_2 and β_3 (Figure 3). The components of stress are determined by the condition that the change in the free energy

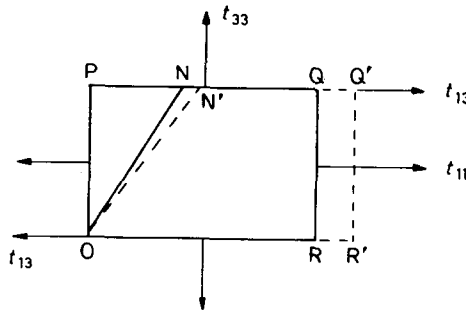


Figure 3

[†]The proof is essentially that given in ref. 10 for the three-chain network model. This relationship is equivalent to the property of an ellipsoid, that the sum of the squares of any three conjugate diameters is equal to the sum of the squares of its principal axes¹³. Any three mutually perpendicular diameters of an unstrained sphere become conjugate diameters of the ellipsoid in the strained state.

in an incremental strain is equal to the work done by the applied forces.

Normal stress t_{11} —Consider the displacement of the surface QR (*Figure 3*) through the distance $\delta\beta_1$ to the parallel position Q'R', at constant β_2 and β_3 . This displacement involves a change in the shear strain of amount $\delta\gamma$ in addition to the change in β_1 . To find $\delta\gamma$, consider the line ON which was parallel to OZ in the unstrained state; this will move to ON' as a result of the additional strain. Since the strain is uniform

$$NN'/PN = QQ'/PQ = \delta\beta_1/\beta_1 \quad (58)$$

Also, since $OP = \beta_3$,

$$PN = \beta_3\gamma, \quad NN' = \beta_3\delta\gamma \quad (59)$$

Hence

$$\delta\gamma = (\gamma/\beta_1) \delta\beta_1 \quad (60)$$

The change in free energy is therefore [from equation (57)]

$$\delta A = \delta A^* + G' [\beta_1 + \beta_3^2\gamma (\gamma/\beta_1)] \delta\beta_1 \quad (61)$$

where

$$\delta A^* = (dA^*/dV) \delta V = -p^* \beta_2\beta_3 \delta\beta_1 \quad (62)$$

The mechanical work δW is given by

$$\delta W = t_{11}\beta_2\beta_3 \delta\beta_1 \quad (63)$$

From equations (61), (62) and (63)

$$t_{11}\beta_2\beta_3 = -p^*\beta_2\beta_3 + G' (\beta_1 + \beta_3^2\gamma^2/\beta_1)$$

or, since $\beta_1\beta_2\beta_3 = V$,

$$t_{11} = -p^* + (G'/V) (\beta_1^2 + \beta_3^2\gamma^2) \quad (64)$$

Normal stress t_{22} —Since β_2 is the principal axis the equations for the principal stresses³ apply. Hence

$$t_{22} = -p^* + (G'/V) \beta_2^2 \quad (65)$$

Normal stress t_{33} —Consider a displacement of the surface PQ (*Figure 3*) through a distance $\delta\beta_3$ parallel to OZ. In this case PN remains constant but OP increases. Hence

$$\delta\gamma = \delta(PN/OP) = -(\gamma/\beta_3) \delta\beta_3 \quad (66)$$

Therefore

$$\delta A = -p^*\delta V + G' [\beta_3(1 + \gamma^2) + \beta_3^2\gamma(-\gamma/\beta_3)] \delta\beta_3$$

or

$$\delta A = [-p^*\beta_1\beta_2 + G'\beta_3] \delta\beta_3 \quad (67)$$

The mechanical work is

$$\delta W = t_{33}\beta_1\beta_2 \delta\beta_3 \quad (68)$$

Hence

$$t_{33} = -p^* + (G'/V) \beta_3^2 \quad (69)$$

From equations (64) and (65)

$$t_{11} - t_{22} = (G'/V) (\beta_1^2 - \beta_2^2 + \beta_3^2\gamma^2) \quad (70)$$

Tangential stress t_{13}

In an increment of shear strain $\delta\gamma$ at constant β_1 , β_2 and β_3 , the surface B"D" (Figure 2) is displaced horizontally through a distance $OB\delta\gamma$ or $\beta_3\delta\gamma$. The area of this surface being $\beta_1\beta_2$, the work done is thus

$$\delta W = t_{13}\beta_1\beta_2 \cdot \beta_3\delta\gamma \quad (71)$$

Since the volume is unchanged $\delta A^* = 0$ and the change in free energy is, from (57)

$$\delta A = G'\beta_3^2\delta\gamma \quad (72)$$

Equating δA and δW

$$t_{13} = G' (\beta_3^2 / \beta_1\beta_2\beta_3)\gamma = (G' / V)\beta_3^2\gamma \quad (73)$$

In the present case the unstrained volume was taken as unity. For the general case of an unstrained volume V_u we have $V/V_u = \beta_1\beta_2\beta_3$ and equation (73) may be written

$$t_{13} = (G' / V_u) (\beta_3 / \beta_1\beta_2)\gamma \quad (73a)$$

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