Thermomechanics of rubber at small strains

R. E. Lyon* and R. J. Farris
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

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A reduced variable, linear thermoelastic constitutive equation for rubber at small strains is obtained from classical linear thermoelasticity and empirical observations about the stress–temperature behaviour of real elastomers at fixed strain. In contrast to the statistical theory of rubber elasticity, volume changes are recognized explicitly in the three constant equation of state. This formulation leads to self-consistent, quantitative predictions of the thermoelastic inversion and internal energy changes with deformation which support the basic tenets of the statistical theory.

(Keywords: rubber elasticity; thermoelasticity; thermomechanics; internal energy; entropy; rubber)

Considerable effort has been expended to measure and derive relationships for the internal energy and entropy contributions to the deformation behaviour of rubber solids. The constitutive equation most commonly used to interpret thermoelastic data and derive internal energy and entropy expressions for rubbery solids is that obtained from the statistical theory of rubber elasticity. This is a single parameter equation in the temperature dependent shear modulus $G=NkT$, with N the number of network chains per unit volume, k the Boltzmann constant, and T the absolute temperature. Consequently, all of the temperature dependence (and none of the volume dependence) of the ideal rubbery solid is contained in the single mechanical constant, $G(T)$. The assumption of constant volume deformation (i.e. incompressibility) is very nearly true for rubber, and is convenient for large deformation strain energy formulations since it greatly simplifies the relationship between the three principal extensions. However, this type of formulation cannot account in a self-consistent manner for dilatational effects caused by deformation which are thought to be the primary source of the internal energy contribution to rubber deformation at small strains where the statistical theory is assumed to be valid.

Internal energy changes resulting from volume changes cannot be calculated directly from the one parameter ideal rubber equation of state which recognizes only distortional contributions to the free energy. The usual procedure for circumventing this deficiency of the statistical theory is to invoke a thermodynamic correction term which relates stress to volume and ultimately to internal energy[1]. More unified continuum derivations by Chadwick[2] and Crochet and Naghdi[3] simultaneously recognize the bulk, liquid-like behaviour of rubber and the distortional network contribution in the free energy function for rubber-like materials. These formulations lead naturally to the prediction of anomalous behaviour such as the thermoelastic inversion and can account in a general sense for the internal energy changes with deformation.

Along similar lines, Boggs[4] derived a partition function for rubber which is the product of the partition function of a liquid comprised of chain elements and the partition function of the non-interacting network chains. The total free energy was then the sum of the free energy of the network without intermolecular interactions and the free energy of the liquid in which intermolecular interactions were recognized explicitly through (for example) a Van der Waals potential. A result of Boggs' work, which is particularly relevent to the following discussion, is the predicted volume–temperature relationship for rubber, which shows slight negative deviation from linearity, i.e. the thermal expansion coefficient is expected to be roughly proportional to T_0/T, where T_0 is a reference temperature.

In the following section thermodynamic relationships for elastic solids (see Appendix) will be used with the constitutive equation for a classical linear thermoelastic solid to review the calculation of internal energy and entropy changes with deformation for hard elastic solids. Finally, empirical observations about the thermoelastic behaviour of rubbery solids will lead to a linear thermoelastic constitutive equation which includes temperature depencence in the form of a reduced modulus and thermal expansion coefficient. Using this constitutive equation for rubber at small strains, internal energy changes are calculated which agree with the assumptions of the statistical theory and show quantitative agreement with experiment.

CLASSICAL LINEAR THERMOELASTICITY

The general thermodynamic equations for elastic solids given in the Appendix provide the necessary relationships to deduce internal energy and entropy contributions to elastic deformation provided a suitable constitutive equation for the solid is known. In this section we follow closely the derivation of Sneddon[5] using the constitutive equation for a classical linear thermoelastic solid, i.e. a solid whose properties are assumed to be independent of temperature.

The constitutive equation relating the stress, strain and

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* Present address: Lawrence Livermore National Laboratory, PO Box 808, L-338, Livermore, CA 94550, USA.

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temperature of an isotropic, linear thermoelastic solid can be written

$$\sigma_{ij}=\frac{E_T}{(1+v)(1-2v)}[ve\delta_{ij}+(1-2v)\varepsilon_{ij}-(1+v)\,\alpha_T(T-T_o)\delta_{ij}] \tag{1}$$

where ε_{ij} are the components of the small strain tensor,

$$\varepsilon_{ij}=\tfrac{1}{2}\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right] \tag{2}$$

E_T is the temperature-independent Young's modulus, and α_T the temperature-independent linear thermal expansion coefficient at constant stress. The dilatation, e, is $e=\varepsilon_{ii}=\partial V/V_o$ and v is Poisson's ratio. Equation (1) can be contracted showing that the mean normal pressure, p, is

$$p=-\tfrac{1}{3}\sigma_{kk}=\frac{-E_T}{3(1-2v)}[e-3\alpha_T(T-T_o)] \tag{3}$$

from which

$$K_T=-\left(\frac{\partial P}{\partial e}\right)_T=\frac{E_T}{3(1-2v)} \tag{4}$$

is the isothermal bulk modulus for the solid whose constitutive equation is equation (1).

From equations (1) and (46) (see Appendix), the change in internal energy with strain for such a solid is

$$\left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_T=\frac{E_T}{(1+v)(1-2v)}[ve\delta_{ij}+(1-2v)\varepsilon_{ij}+(1+v)\,\alpha_T T_o\delta_{ij}] \tag{5}$$

Substituting equations (50) and (5) into the total differential for the internal energy (equation (47)) and integrating gives

$$U-U_o=\tfrac{1}{2}\sigma_{ij}\varepsilon_{ij}+\frac{E_T\alpha_T e}{2(1-2v)}(T+T_o)+C_\varepsilon(T-T_o), \tag{6}$$

where U_o denotes the internal energy of the initial state $\varepsilon_{ij}=0$, $T=T_o$. The last term on the right hand side of equation (6) is the heat content, and the middle term results from the interaction of elastic deformation and thermal diffusion.

The entropy change is derived analogously. From equations (45) and (1), the change in entropy with strain at constant temperature is

$$\left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T=\frac{E_T\alpha_T}{1-2v}\delta_{ij} \tag{7}$$

The total differential for the entropy in terms of the strain and temperature is

$$\mathrm{d}S=\left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T\mathrm{d}\varepsilon_{ij}+\left(\frac{\partial S}{\partial T}\right)_{\varepsilon_{ij}}\mathrm{d}T, \tag{8}$$

which together with equations (50) and (7), and integration gives for the entropy change

$$S-S_o=\frac{E_T\alpha_T}{1-2v}e+C_\varepsilon\ln\frac{T}{T_o} \tag{9}$$

The second term on the right hand side of equation (9) is the entropy change due to heat conduction alone, while the first term arises from the coupling of elastic and thermal processes. For a deformation process at constant temperature $T=T_o$, it is seen that the entropy change is the result of volume dilatation.

If the coordinate axes are chosen such that the strains are in the principal directions, $e=\varepsilon_1+\varepsilon_2+\varepsilon_3$, and $v=-\varepsilon_2/\varepsilon_1$, so that for uniaxial deformation in the 1 direction at constant temperature $T=T_o$,

$$\varepsilon_1=\frac{e}{1-2v}\qquad \sigma_1=E_T\varepsilon_1$$

and the internal energy change for the isothermal uniaxial deformation at constant pressure becomes

$$U-U_o=T_oE_T\alpha_T\varepsilon_1+\tfrac{1}{2}E_T\varepsilon_1^2 \tag{10}$$

which is quadratic in strain. The two terms which contribute to the internal energy change depend on E_T, which represents essentially the harmonic character of the binding forces, and α_T, which is associated with the anharmonicities.

From equation (9) it is clear that the reversible heat of an isothermal tensile deformation process at constant pressure is

$$q=T_o(S-S_o)=T_oE_T\alpha_T\varepsilon_1 \tag{11}$$

This equation has been verified by deformation calorimetry of steel wires[6] and glassy and crystalline polymers[7,8]. The relationship between the heat, work and internal energy change for a linear thermoelastic solid in uniaxial deformation at constant temperature and pressure is shown in *Figure 1*.

The above derivations showed that, in the final analysis, volume changes determine the entropy contribution and influence the internal energy component of deformation for classical linear thermoelastic solids. In many cases, particularly in rubber elasticity, it is desired to separate the internal energy contributions arising from shape or length changes from

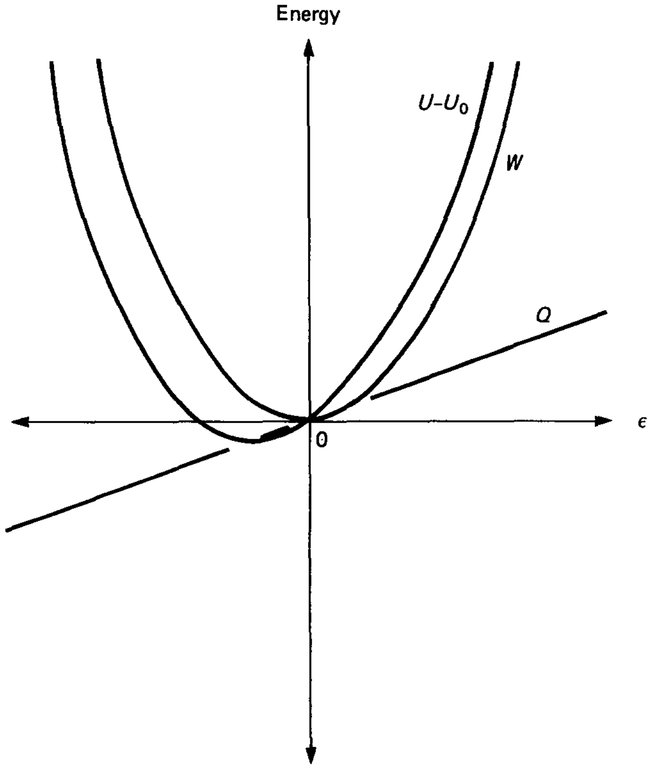

Figure 1 Heat, work and internal energy change *versus* strain for a classical linear thermoelastic solid

those due to volume changes. Shape and volume changes can be considered separately by writing the stress and strain tensors in terms of their deviatoric (shape) and spherical (volumetric) components. Using this formulation, the stress components become

$$\sigma_{ij} = \sigma'_{ij} + p\delta_{ij}, \tag{12}$$

where primes denote the deviatoric components and p is the mean normal pressure given by equation (3). Similarly, the strain components become

$$\varepsilon_{ij} = \varepsilon'_{ij} + \tfrac{1}{3}e\delta_{ij} \tag{13}$$

Substituting for the stress and strain components in equation (1), the constitutive equation for the classical linear thermoelastic solid in terms of the deviatoric stress and strain becomes simply

$$\sigma'_{ij} = 2G_T\varepsilon'_{ij} \tag{14}$$

and

$$\left(\frac{\partial \sigma'_{ij}}{\partial T}\right)_{\varepsilon_{pq}} = 0 \tag{15}$$

for a material having a temperature independent shear modulus, G_T. The internal energy change due only to shape changes at constant temperature then becomes

$$\left(\frac{\partial U}{\partial \varepsilon'_{ij}}\right)_T = \sigma'_{ij} - T\left(\frac{\partial \sigma'_{ij}}{\partial T}\right)_{\varepsilon_{pq}} = \sigma'_{ij} \tag{16}$$

The ratio of the energetic component, $(\partial U/\partial \varepsilon'_{ij})_T$, to the deviatoric stress for the linear thermoelastic solid is

$$\frac{1}{\sigma'_{ij}}\left(\frac{\partial U}{\partial \varepsilon'_{ij}}\right)_T = 1 \tag{17}$$

Consequently, in the absence of volume changes, the energetic component of the elastic stress is identical to the stress for a classical linear thermoelastic solid having temperature independent properties whose constitutive equation is equation (1).

EXTENSION OF LINEAR THERMOELASTICITY TO RUBBERY SOLIDS

As a starting point in developing a suitable constitutive equation for a rubbery solid we assume that at infinitesimal strains rubber behaves like a classical linear thermoelastic solid. However, we relax the restriction of temperature independent properties and allow: $E = E(T)$, $\alpha = \alpha(T)$. From equation (1), the uniaxial stress–strain–temperature equation for a linear solid is, with $\sigma_{11} = \sigma$, $\sigma_{22} = \sigma_{33} = 0$, and $\varepsilon_{11} = \varepsilon$,

$$\sigma = E\,[(\varepsilon - \alpha(T - T_o)] \tag{18}$$

Experiments show that the stress–temperature behaviour of rubber at constant strain is linear (i.e. has a constant slope) over a wide range of temperature, but that it is a function of strain, going from negative to positive with increasing strain. This behaviour is clearly illustrated in *Figure 2* which shows stress–temperature data for natural rubber at various fixed extension ratios ($\lambda = L/L_o$) obtained by Shen and Blatz[9].

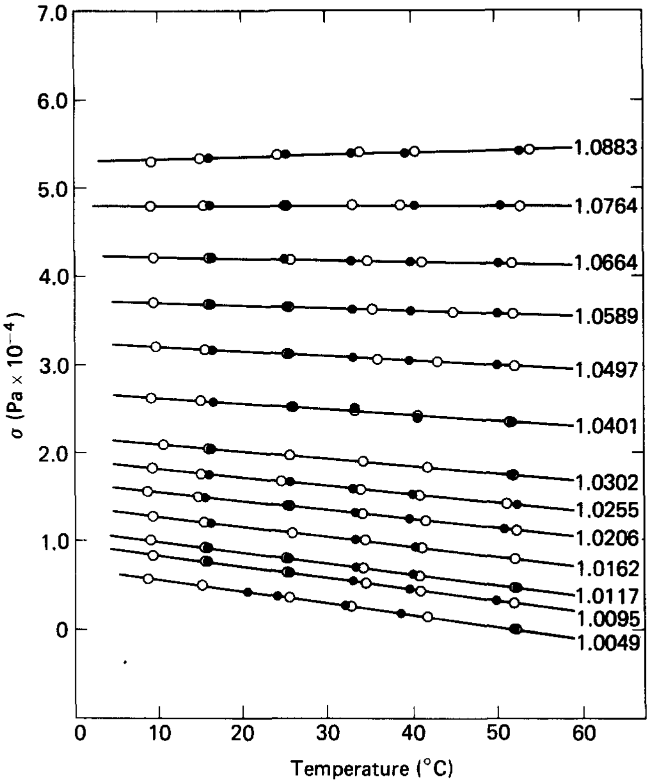

Figure 2 Stress–temperature data of Shen and Blatz for natural rubber held at various extension ratios, $\lambda = 1 + \varepsilon$. (●) heating cycle, (○) cooling cycle

With both a temperature dependent modulus and thermal expansion coefficient in equation (18), differentiating the stress with respect to temperature at constant strain gives

$$\left(\frac{\partial \sigma}{\partial T}\right)_\varepsilon = \left(\frac{\partial E}{\partial T}\right)_\varepsilon \varepsilon - E\alpha - (T - T_o)\frac{\partial}{\partial T}(E\alpha) \tag{19}$$

As a consequence of the temperature independent slope

$$\left(\frac{\partial E}{\partial T}\right)_\varepsilon \neq f(T) \tag{20}$$

$$E\alpha \neq f(T) \tag{21}$$

From the statistical theory of rubber elasticity and linear elasticity we know that $E(T) = 2(1+\nu)G(T) = E_oT/T_o$ (which satisfies equation (20)). One possible choice for $\alpha(T)$ which satisfies equations (19) and (21) is $\alpha(T) = \alpha_oT_o/T$, where $\alpha_o \equiv \alpha(T_o)$ and $E_o \equiv E(T_o)$. Using these expressions for $\alpha(T)$ and $E(T)$ the stress–temperature slope at constant strain from equations (18) and (19) is

$$\left(\frac{\partial \sigma}{\partial T}\right)_\varepsilon = \frac{E_o}{T_o}\varepsilon - \alpha_oE_o \tag{22}$$

which is independent of temperature and is a linear function of strain, being negative at small strains and positive at large strains as is observed experimentally.

At the thermoelastic inversion, the stress–temperature slope of rubber is zero. Setting the left hand side of equation (22) to zero, it is found that the thermoelastic inversion occurs when $\varepsilon = \alpha_oT_o$. From equation (22) and the relationship between shear and tensile moduli, it follows that Poisson's ratio is also independent of temperature.

Substituting $E(T) = E_oT/T_o$, and $\alpha(T) = \alpha_oT_o/T$ in the constitutive equation for the classical linear thermoelastic solid yields the following three dimensional constitutive equation for rubber at infinitesimal strains

$$\sigma_{ij}=\frac{E_o T/T_o}{(1+v)(1-2v)}\left[ve\delta_{ij}+(1-2v)\varepsilon_{ij}-(1+v)\alpha_o T_o\left(1-\frac{T_o}{T}\right)\delta_{ij}\right] \tag{23}$$

Using equation (23) with the thermodynamic relationships given in the Appendix, we obtain the following results for the internal energy and entropy changes in a rubber-like material, which we now define as a linear thermoelastic solid with temperature dependent properties

$$\left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_T=\frac{E_o T_o \alpha_o}{1-2v}\delta_{ij} \tag{24}$$

$$\left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T=\left(\frac{-\partial \sigma_{ij}}{\partial T}\right)_{\varepsilon_{pq}}=\frac{-\sigma_{ij}}{T}+\frac{E_o \alpha_o T_o}{T(1-2v)}\delta_{ij} \tag{25}$$

Upon substitution into the respective total differentials, using the previously derived temperature dependence, integrating gives for the internal energy and entropy change of rubber

$$U-U_o=\frac{E_o T_o \alpha_o}{1-2v}e+C_\varepsilon(T-T_o) \tag{26}$$

$$S-S_o=-\frac{1}{T}\left[\tfrac{1}{2}\sigma_{ij}\varepsilon_{ij}-\frac{E_o T_o \alpha_o}{1-2v}e\right]+C_\varepsilon \ln\frac{T}{T_o} \tag{27}$$

At constant volume, and temperature $T=T_o$ it is seen that $U-U_o=0$ and $S-S_o=-1/T_o(1/2\,\sigma_{ij}\varepsilon_{ij})$. For comparison with experiment, the uniaxial form of equations (26) and (27) are, at constant pressure and temperature $T=T_o$,

$$U-U_o=E_o T_o \alpha_o \varepsilon_1 \tag{28}$$

$$Q=T_o(S-S_o)=E_o\alpha_o T_o\varepsilon_1-\tfrac{1}{2}E_o{\varepsilon_1}^2 \tag{29}$$

and

$$W=A-A_o=(U-U_o)-T_o(S-S_o)=\tfrac{1}{2}E_o{\varepsilon_1}^2 \tag{30}$$

The heat, work and internal energy for rubber at small strains predicted by equations (28)–(30) are shown schematically in *Figure 3*. The form of these functions has been confirmed several times for natural rubber using deformation calorimetry[10–12]. In particular the heat goes through an inversion at $\varepsilon_1=2\alpha_o T_o$, while the internal energy is found to be a linear function of strain at constant temperature and pressure, this being a result of the linear relationship between strain and dilatation at small strains.

Volume and shape contributions to the internal energy and entropy changes in rubber during deformation can be separated by considering the principal stress difference, $\sigma_{11}-\sigma_{22}$, which removes the volume dependent terms for a uniaxial experiment as is normally done in rubber elasticity formulations. In this way the uniaxial stress becomes, from equation (23)

$$\sigma=\sigma_{11}-\sigma_{22}=\frac{E_o T/T_o}{1+v}(\varepsilon_{11}-\varepsilon_{22})=2G_o T/T_o(\varepsilon_{11}-\varepsilon_{22}) \tag{31}$$

But since $\varepsilon_{22}=(e-\varepsilon_{11})/2$,

$$\begin{aligned}\sigma&=3G_o T/T_o(\varepsilon_{11}-e/3)\\&=3G_o T/T_o\varepsilon'_{11}\end{aligned} \tag{32}$$

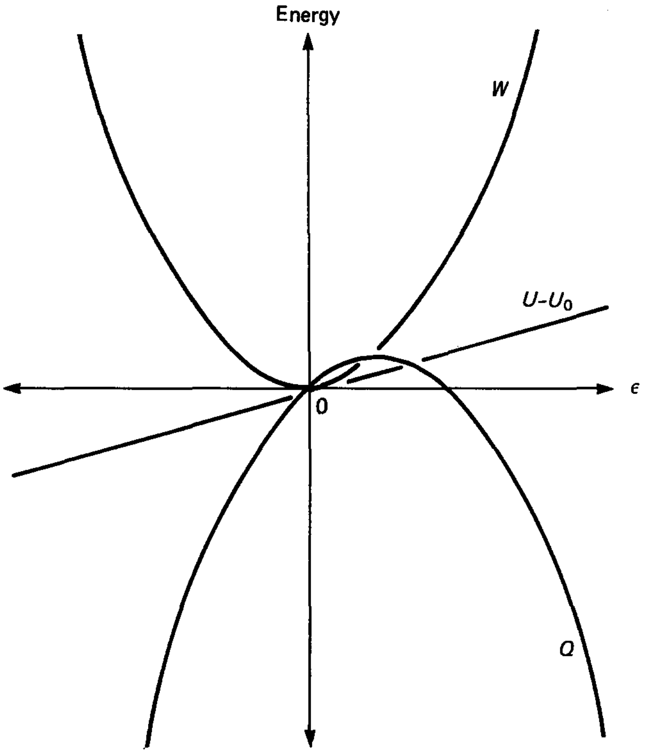

Figure 3 Heat, work and internal energy change *versus* strain for a linear rubbery solid

and the stress–temperature coefficient is

$$\left(\frac{\partial\sigma}{\partial T}\right)_{\varepsilon'_{11}}=\frac{3G_o}{T_o}\varepsilon'_{11}=\frac{\sigma}{T} \tag{33}$$

Introducing the notation used in the literature of rubber thermodynamics, the internal energy change with strain at constant temperature and volume should be

$$F_e=\left(\frac{\partial U}{\partial \varepsilon'_{11}}\right)_T=T\left[\frac{\sigma}{T}-\left(\frac{\partial\sigma}{\partial T}\right)_{\varepsilon'_{11}}\right]=0 \tag{34}$$

The energetic component of the stress arising solely from shape or length changes at small strain and constant pressure in a ratio with the stress ($\sigma=f$) is therefore

$$\frac{f_e}{f}\equiv\frac{1}{\sigma}\left(\frac{\partial U}{\partial\varepsilon_{11}}\right)_{T,V}=\frac{1}{\sigma}\left(\frac{\partial U}{\partial\varepsilon'_{11}}\right)_T=0 \tag{35}$$

in agreement with the definition of an ideal rubber exhibiting no volume changes during deformation.

COMPARISON WITH EXPERIMENT

Experiments by Gee, Stern and Treloar[13] show reasonable agreement between measured dilatation and that calculated from equation (26) using internal energy changes obtained from stress–temperature data of natural rubber at constant pressure. Gee[14] obtained equation (26) in differential form, $(\partial U/\partial e)_T$, by assuming the relationship between internal energy and volume for a material under hydrostatic pressure to hold when the volume change is due to a tensile stress. Thermostatic measurements on natural rubber in shear by Meyer and van der Wyk[15] at small strains showed no thermoelastic inversion and a negligible energetic component to the stress, since shear strain involves no volume changes.

For direct comparison with equation (28), we cite the uniaxial stress–temperature data at constant (atmos-

Table 1 $(\partial U/\partial \varepsilon_1)_{T_0,P}$ values

λ_1	$\left(\frac{\partial U}{\partial \varepsilon_1}\right)_{T_0,P} \times 10^{-4}$ Pa Measured	Calculated	$\frac{1}{\sigma}\left(\frac{\partial U}{\partial \varepsilon_1}\right)_{T_0,P}$ Measured	Calculated
1.0049	4.23	4.34	13.23	13.56
1.0095	4.28	–	7.13	7.23
1.0117	4.30	–	5.66	5.71
1.0162	4.34	–	4.06	4.06
1.0206	4.31	–	3.15	3.17
1.0255	4.32	–	2.62	2.63
1.0302	4.39	–	2.25	2.23
1.0401	4.39	–	1.74	1.72
1.0497	4.46	–	1.42	1.39
	$\langle x\rangle = 4.34 \pm 0.07$			

pheric) pressure for natural rubber at infinitesimal strains obtained by Shen and Blatz[9]. These authors report $\alpha_0 = 2.2 \times 10^{-4}$/K at $T_0 = 303$ K, and we calculate $E_0 = 0.651$ MPa from the data at strains up to 0.03. The change in internal energy with tensile strain at constant pressure should then be

$$\left(\frac{\partial U}{\partial \varepsilon_1}\right)_{T_0,P} = E_0 T_0 \alpha_0 = (0.651 \times 10^6 \text{ Pa})(303 \text{ K})(2.2 \times 10^{-4} \text{ K}^{-1})$$
$$= 4.34 \times 10^4 \text{ Pa}$$

In *Table 1* the values of $(\partial U/\partial \varepsilon_1)_{T_0,P}$ evaluated at each strain for temperature $T = T_0$ are shown using equation (46) and the reported stress–temperature data. It is seen that at small strains, where the linear theory is expected to hold, reasonable agreement with the measured value is achieved. The ratio $\frac{1}{\sigma}\left(\frac{\partial U}{\partial \varepsilon_1}\right)_{T_0,P}$ calculated with the measured stress is also compared to values for this quantity obtained from the thermoelastic data. Again, good agreement is obtained at small strains where $\varepsilon_1 = \lambda_1 - 1$ and λ_1 is the extension ratio.

According to equation (22), the thermoelastic inversion should occur at $\varepsilon_1 = \alpha_0 T_0 = 0.067$. This compares favourably with the value of $\varepsilon_1 = 0.070$ obtained from the data of Shen and Blatz, considering the limitations of the small strain theory.

The form of the thermal expansion coefficient leading to equation (23), i.e. $\alpha(T) = \alpha_0 T_0/T$, suggests slight negative curvature in a plot of volume *versus* temperature, as predicted by Boggs. Moreover both the thermal expansion coefficient and the modulus are assumed to be temperature dependent material properties which are independent of deformation state. Experiments on natural rubber by Allen, Bianchi and Price[16] confirm that α_0 is independent of uniaxial strain in the range $\lambda_1 = 1.0$–2.2.

CONCLUSIONS

A linear thermoelastic constitutive equation for rubber at small strains is obtained by generalizing classical linear thermoelasticity to include a temperature dependent modulus and thermal expansion coefficient. From this constitutive equation it was shown that the internal energy change in rubbery solids is the result of dilatation while the distortional strain energy resides in the entropy change. This behaviour is in contrast to hard elastic solids but in complete agreement with statistical and molecular theories of rubber elasticity. Consequently, the temperature dependent modulus and thermal expansion coefficient of rubber reverses the role of internal energy and entropy contributions to deformation at small strains.

Quoting from Gee's 1946 paper on natural rubber, 'We conclude therefore that for small extensions, the observed expansion is produced by the hydrostatic component of the tensile force. It consists of an increase in the average intermolecular spacing, and is accompanied by the equivalent increase in both internal energy and entropy.'

APPENDIX

General thermodynamic relations for elastic solids

The first law of thermodynamics which describes the complete energy balance for any closed deformation process, whether reversible or irreversible, has the well known form

$$dU = dq + dw \qquad (36)$$

where dU, dq and dw are the incremental changes in internal energy, heat and work per unit volume.

The incremental work may be due to changes in any relevant extensive–intensive mechanical variable pair representing generalized forces and displacements. For homogeneous solid deformation, the work per unit volume is

$$dw = \sigma_{ij} d\varepsilon_{ij} \qquad (37)$$

where σ_{ij}, ε_{ij} $(i, j = 1, 2, 3)$ are components of compatible stress and strain tensors. With equation (37) the first law of thermodynamics for solid deformation becomes,

$$dU = dq + \sigma_{ij} d\varepsilon_{ij} \qquad (38)$$

The second law of thermodynamics gives the entropy balance, S, at constant temperature, T,

$$dS \geq \frac{dq}{T} \qquad (39)$$

where the inequality holds for spontaneous or irreversible processes and the equality for reversible processes.

For a reversible deformation process, the combined first and second laws give

$$dU = TdS + \sigma_{ij} d\varepsilon_{ij} \qquad (40)$$

The Helmholtz free energy, A, is

$$A = U - TS \qquad (41)$$

which toegether with equation (40) yields

$$dA = \sigma_{ij} d\varepsilon_{ij} - SdT \qquad (42)$$

From equation (42) it follows that

$$\left(\frac{\partial A}{\partial \varepsilon_{ij}}\right)_T = \sigma_{ij} \qquad (43)$$

and

$$\left(\frac{\partial A}{\partial T}\right)_{\varepsilon_{ij}} = -S \qquad (44)$$

from which

$$\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\varepsilon_{kl}} = -\left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T \qquad (45)$$

From equations (40) and (45),

$$\left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_T = \sigma_{ij} - T\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\varepsilon_{pq}} \qquad (46)$$

Writing the total differential for the internal energy in terms of the strain and temperature,

$$\mathrm{d}U = \left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_T \mathrm{d}\varepsilon_{ij} + \left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}} \mathrm{d}T \qquad (47)$$

and rearranging equation (40) to read

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U - \frac{1}{T}\sigma_{ij}\mathrm{d}\varepsilon_{ij} \qquad (48)$$

the incremental entropy change with equation (47) in (48) is

$$\mathrm{d}S = \frac{1}{T}\left[\left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_T \mathrm{d}\varepsilon_{ij} + \left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}} \mathrm{d}T\right] - \frac{1}{T}\sigma_{ij}\mathrm{d}\varepsilon_{ij} \qquad (49)$$

from which it follows that

$$T\left(\frac{\partial S}{\partial T}\right)_{\varepsilon_{ij}} = \left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}} = C_\varepsilon \qquad (50)$$

Subscripts ε_{ij} on all of the above partial differential equations imply that all strains are held constant. In equation (50), C_ε is the heat capacity of the solid at constant strain. In the undeformed state, $C_\varepsilon = C_v$.

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