

## NOTES

### ***On the Thermoelastic Effect and Configurational Entropy in Rubber-Like Solids***

The thermoelastic effect in solids, first predicted by Thompson and studied by Joule<sup>1</sup> and others,<sup>3c</sup> is well known. In particular, the anomalous behavior of rubber has been extensively studied. Treloar<sup>2</sup> and Flory<sup>3</sup> discuss this and related topics, and James and Guth<sup>4</sup> have derived theoretical relationships from statistical theory.

Thompson's equation describing the temperature change in a solid on the application of stress is simply derived as follows: Since entropy is an extensive property we may write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (1)$$

For a reversible adiabatic change,  $dS = 0$ ; therefore,

$$dT = -\frac{(\partial S/\partial P)_T dP}{(\partial S/\partial T)_P} = \frac{V\gamma T dP}{C_p}$$

where  $\gamma$  is the volume expansion coefficient of the solid and  $C_p$  is the heat capacity at constant pressure. It is readily shown that, for uniaxial stress,  $\gamma dP$  may be replaced by  $-\alpha d\sigma$  ( $\alpha$  = linear expansion coefficient and  $\sigma$  = uniaxial tensile stress).

This leads to the original form of the Thompson relationship  $dT = -\alpha T d\sigma/\rho s$  ( $\rho$  = density,  $s$  = specific heat) or, since the term  $\alpha/\rho s$  is substantially constant with stress,

$$\Delta T = -\frac{\alpha T \Delta \sigma}{\rho s}$$

Equation (1) implies that, in reversible adiabatic expansion, entropy change arising due to a change in internal pressure is compensated by a temperature change just sufficient to produce a numerically equal and opposite entropy change, fulfilling the condition of a zero total change in the entropy of the system.

In the case of a rubber-like solid, however, adiabatic extension produces an alignment of the polymer chains which represents an ordering process and results in a negative contribution to the total entropy of the system. Let us postulate that the change in entropy due to applied uniaxial, tensile stress under isothermal conditions  $dS' = (\partial S/\partial \sigma)_T d\sigma$  may be represented as the sum of two terms:

$$dS' = dS_0 + dS_c$$

where  $dS_0$  is the change in entropy due to the change in internal pressure and volume\* and  $dS_c$  is the configurational entropy change resulting from chain ordering. Applying this postulate to eq. (1) in its uniaxial form,

$$dS = \left(\frac{\partial S}{\partial T}\right)_\sigma dT + \left(\frac{\partial S_0}{\partial \sigma}\right)_T d\sigma + \left(\frac{\partial S_c}{\partial \sigma}\right)_T d\sigma \quad (2)$$

Apply the same relationship as before and  $dS = 0$  for a reversible adiabatic change:

$$dT = -\frac{\alpha T d\sigma}{\rho s} - \frac{T}{C_p} \left(\frac{\partial S_c}{\partial \sigma}\right)_T d\sigma \quad (3)$$

Further, let us assume that  $\sigma/\rho s$  is substantially constant and has the value  $\alpha_0/\rho_0 s_0$ , where the subscript zero refers to the zero stress values of the parameters.

Using eq. (3) and experimental values of  $\Delta T$ , the thermoelastic temperature change, it should

\* Note: Flory has indicated that errors ensue by using constant pressure assumption due to changes in internal pressure and prefers to assume constant volume. Since there are volume changes, no assumptions of constant pressure or volume are implied.

now be possible to calculate the value of  $\Delta S_c$  [ $= (\partial S_c / \partial \sigma)_T d\sigma$ ] for a range of stress values. This has been done using experimental values from the literature<sup>2,4,5</sup> for natural rubber vulcanizate. Zero stress values of specific heat, density, and expansion coefficient were obtained from reference 6. Room temperature of 298 K was assumed.

We have been unable to obtain experimental values of  $\Delta S_c$  for comparison. Flory,<sup>3</sup> however, derives an expression for the change in configurational entropy with stress by a statistical approach:

$$\Delta S_c = -\frac{k\nu_e}{2} \left( a^2 + \frac{2}{a} - 3 \right) \quad (4)$$

where  $a$  is the extension ratio,  $k$  is Boltzmann's constant, and  $\nu_e$  is the number of effective crosslinkages in the system. A comparison of the values of  $\Delta S_c$  from eq. (4) with  $\nu_e = 1.35 \times 10^{22}$  gave reasonable agreement with values derived from eq. (3) at very low extensions but values which were higher than the values obtained from eq. (3) at moderate extensions ( $a = 1.5$ – $4.0$ ). Flory<sup>3a</sup> remarks, however, that chain entanglement (which leads to effective crosslinkages) may change, and in fact decrease, with time but that as yet there is no theoretical basis by which this time-dependent change may be calculated. It seems reasonable to assume that chain entanglements which are known to

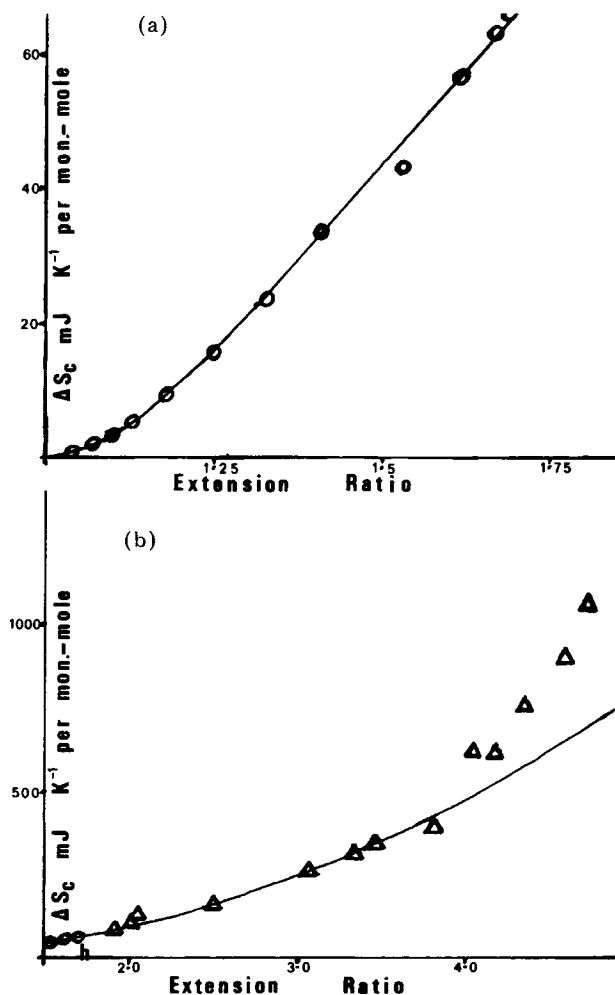


Fig. 1. Configurational entropy. Continuous lines, theoretical calculation using eqs. (3), (4), and (5): (a) (O from eq. (3) using the data points of Dart<sup>3</sup>; (b) ( $\Delta$ ) from eq. (3) using the data points of Dart, Anthony, and Guth.<sup>5</sup>

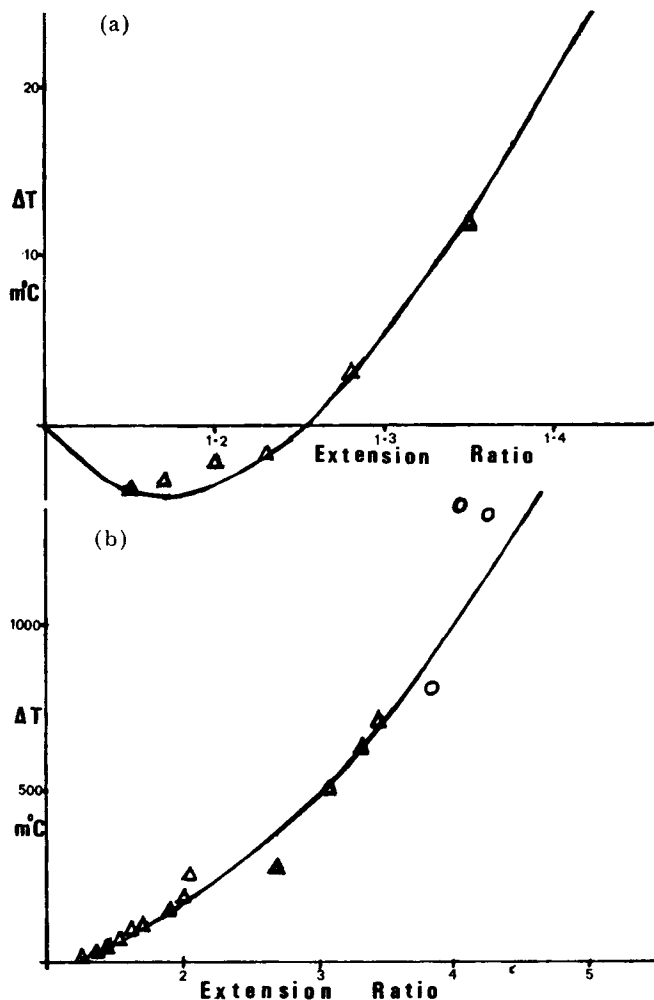


Fig. 2. Thermoelastic temperature change. Continuous lines in (a) and (b), theoretical prediction, eq. (6): (O) data points of Dart<sup>3</sup>; ( $\Delta$ ) data points of Dart, Anthony, and Guth.<sup>5</sup>

give rise to "effective" crosslinkages thus contributing to the value of  $\nu_e$  could also be modified by the application of uniaxial stress and be modified in such a way as to decrease the value of  $\nu_e$ . It is likely that crosslinkages contributing to  $\nu_e$  are of two basic kinds, namely, "permanent" linkages of a chemically-bonded nature ( $\nu_{e0}$ ) and "labile" linkages, due to entanglements, which are capable of being modified or annihilated on stretching, reforming on contraction in a more or less reversible manner ( $\nu'_e$ ). In the absence of a rigorous theory to describe such processes, it would seem reasonable to formulate a semiempirical relationship with a statistical basis of the kind

$$\nu_e = \nu_{e0} + \nu'_e \exp\left(-A \frac{\Delta l}{l}\right) \quad (5)$$

with  $l$  and  $\Delta l$  the initial length and change on extension.

Figures 1(a) and 1(b) show experimentally derived values of  $S_e$  applying eq. (3) to the data points from the curves of Dart (see ref. 4) and Dart, Anthony, and Guth<sup>5</sup> (see also ref. 2). The solid line is the theoretical curve obtained using eq. (4) with  $\nu_e = 5 \times 10^{21} + 1.5 \times 10^{22} \exp[-1.89 (\Delta l/l)]$  per monomer mole.

Values of uniaxial stress at very low extensions (up to  $a = 1.4$ ) were obtained from the relationship  $\sigma = G(a - 1/a^2)$  given by Treloar, where  $G = 3.9 \text{ kg/cm}^2$ . Beyond  $a = 1.4$ , values were read off the

experimental stress-strain curve for natural rubber vulcanizate at relatively low extensions when little hysteresis occurs.<sup>2,7</sup> The theoretical curve is seen to give an excellent fit to the experimental values up to about 300% extension.

Figures 2(a) and 2(b) show the same experimental points plotted in their original form of thermoelastic temperature change compared with the theoretically based expression, i.e.,

$$\Delta T = -\frac{\alpha_0 T \sigma}{\rho_0 s_0} + \frac{kT}{2C_p} \left[ \nu_e e^0 + \nu'_e \exp\left(-A \frac{\Delta l}{l}\right) \right] \left( a^2 + \frac{2}{a} - 3 \right) \quad (6)$$

using the same values of  $\nu_{e0}$ ,  $\nu'_e$ , and  $A$ . The agreement of the above expression with experiment is again excellent.

Naturally, the values of the constants in eq. (5) were chosen to give as good a fit with experiment as possible, but the values assigned to  $\nu_e$  and  $\nu'_e$  are not unduly critical. What is more, they lie well within the expected range for  $\nu_e$  of  $\sim 3 \times 10^{21}$  to  $\sim 3 \times 10^{22}$  per monomer mole.<sup>3b</sup> In this connection, if one isoprene unit in  $n$  is involved in crosslinking due to vulcanization, the number of such "permanent" crosslinkages,  $\nu_{e0}$ , is given by  $\nu_{e0} = N/2n$  per monomer mole. According to Flory,<sup>3b</sup>  $n$  is in the range of 50 to 100 for conventional vulcanized rubber, and the range of expected values for  $\nu_{e0}$  is thus  $(3 \text{ to } 6) \times 10^{21}$  per monomer mole, which is excellent justification for the selected value of  $5 \times 10^{21}$  per monomer mole. If the treatment has any validity, these values imply that there are three times as many "labile" crosslinkages as "permanent" ones.

The above approach offers a method of estimating configurational entropy changes in rubber-like solids by means of comparatively simple thermoelastic measurements and utilizing known material parameters under zero stress. Experimental values of entropy change with stress obtained by some independent method be desirable for comparison; but, nevertheless, the method appears to be promising.

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