The Effects of Strain on the Equilibrium Properties of Rubber Networks

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The coefficients of isothermal compressibility, cubical expansion and thermal pressure, have been measured for lightly crosslinked butyl rubber over a range of temperatures and at several elongations. The "network contribution" to these coefficients is found to be negligibly small as predicted by analyses based on either the Mooney–Rivlin or Gaussian equations of state.

IN DEVELOPING a molecular theory of rubber elasticity[1] it is usually assumed that the free energy of an amorphous lightly crosslinked rubber can be expressed as the sum of two independent terms

$$F = F^* + F_{el} \tag{1}$$

where F_{el} is the network contribution to the free energy, and F^* is the liquid-like contribution which is associated with intermolecular interactions similar to those which arise in simple liquids. The term F^* is assumed to depend only on T and V and not otherwise on strain. Since the volume of a rubber sample is virtually independent of strain[2,3] it is predicted on the basis of equation (1) that the coefficients of expansion ($\beta_{L,P}$), isothermal compressibility ($\kappa_{L,T}$), and thermal pressure ($\gamma_{L,V}$) are insensitive to variations in strain.

Measurements[4] on natural rubber networks in simple elongation carried out at extension ratios up to 2·2 have shown that $\beta_{L,P}$, $\kappa_{L,T}$ and $\gamma_{L,V}$ are constant within an experimental error of one to two per cent. However, in marked contrast, Bianchi and Pedemonte[5] reported that for a silicone rubber and for an ethylene–propylene rubber the thermal pressure coefficients fall by ten per cent as the extension ratio is increased to 1·5. Since equation (1) is one of the basic premises underlying all current theories of the rubbery state, it is important to clarify the issue of the strain dependence of these coefficients. In the present study we have measured $\beta_{L,P}$, $\kappa_{L,T}$, and $\gamma_{L,V}$ for butyl rubber in simple extension over a range of temperatures and at several extension ratios.

EXPERIMENTAL

Materials

Butyl rubber networks were supplied by Dr E. Bannister of Esso Research Ltd. They were prepared by chlorination of raw butyl rubber which contained one to two per cent isoprene. The product was crosslinked by reaction with zinc diethyldithiocarbamate at 140°C for one hour. The excess salt was extracted using acetone in a Soxhlet extractor. The samples were 1 cm thick and sufficiently transparent to be examined optically for flaws. The density of the rubber was 0·927 g cm^{-3} at 25°C.

Measurement of $\beta_{L,P}$ and $\gamma_{L,V}$

Dilatometric methods described by us elsewhere[6] were used to determine these coefficients. Mercury was used as the containing fluid and the samples were held in simple elongation at a fixed length by means of Invar formers which were bonded on to the ends of the samples with Kodak 910 adhesive. Consequently, the overall values of $\beta_{L,P}$ and $\gamma_{L,V}$ for the contents of the dilatometer had to be corrected for the amounts of mercury and Invar included. Experimental errors were assessed in terms of standard deviations from 'least squares' analyses of the results, and the overall experimental error in $\beta_{L,P}$ was estimated to be $\pm$ 1 per cent and in $\gamma_{L,V}$ to be $\pm$ 1½ per cent.

Measurement of $\kappa_{L,T}$

A technique devised by Dr D. Sims[7] was used to determine $\kappa_{L,T}$. A dilatometer containing the sample surrounded by mercury was placed in a pressure vessel such that the mercury meniscus in the dilatometer stem could be observed through a length of glass pressure tubing which formed part of the pressure vessel. Shell Resella 33 oil was used as a hydraulic fluid to transmit pressure to the contents of the dilatometer and the movement of the mercury meniscus was followed under isothermal conditions by means of a cathetometer. The experimental error in $\kappa_{L,T}$ is estimated to be $\pm$ 3 per cent.

RESULTS

Coefficients of cubical expansion were measured from 20° to 50°C at four extension ratios. No curvature of the volume/temperature plots was detected and so an average value for $\beta_{L,P}$ is quoted in *Table 1* at each extension ratio in this temperature interval.

Table 1. $\beta_{L,P}$ for butyl rubber (20° to 50°C)

α	1·00	1·25	1·50	1·80
$10^4\beta_{L,P}$, deg^{-1}	5·57	5·56	5·55	5·49

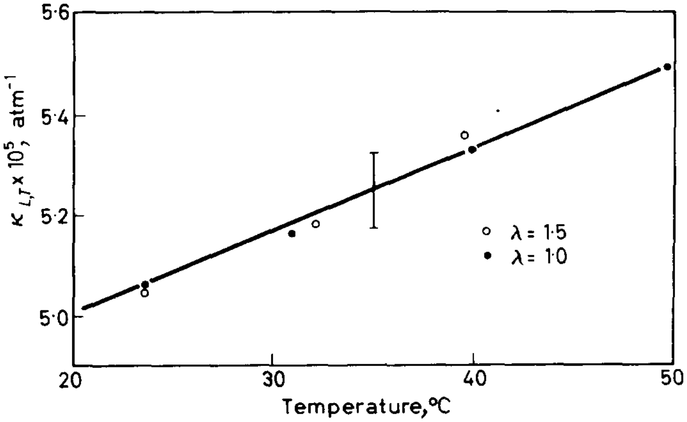

Figure 1—Isothermal compressibilities ($\kappa_{L,T}$)

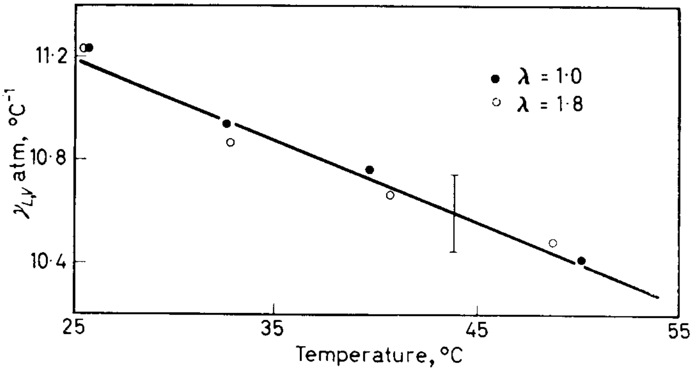

Figure 2—Thermal pressure coefficients ($\gamma_{L,V}$)

Isothermal compressibilities were measured from 20° to 50°C at extension ratios of 1·0 and 1·5, the results are shown in *Figure 1*. *Figure 2* summarizes the results of the direct measurements of thermal pressure coefficients at extension ratios 1·0 and 1·8; the latter results are in satisfactory agreement with indirect values, subject to an overall error of ± 4 per cent, calculated from $\gamma_{L,V} = \beta_{L,P}/\kappa_{L,T}$.

Taken together, the results show that within experimental error the three coefficients are independent of strain over the range covered by our experiments.

DISCUSSION

Using equation (1), together with the standard thermodynamic relationship $P = -(\partial F/\partial V)_{L,T}$, we obtain

$$(\kappa_{L,T})^{-1} = (\kappa^*_T)^{-1} + V \left[\frac{\partial}{\partial V}\left(\frac{\partial F_{el}}{\partial V}\right)_{L,T}\right]_{L,T} \tag{2}$$

$$\gamma_{L,V} = \gamma^*_V - \left[\frac{\partial}{\partial T}\left(\frac{\partial F_{el}}{\partial V}\right)_{L,T}\right]_{L,V} \tag{3}$$

where $\kappa_{L,T}$ and $\gamma_{L,V}$ are the coefficients of isothermal compressibility and thermal pressure for the rubber maintained at constant length L.

The Gaussian theory of rubber elasticity predicts

$$F_{el} = NkT/2\,(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \tag{4}$$

where N is the number of active chains in the network, T the absolute temperature, k the Boltzmann constant and λ the elongation ratio in the direction specified by the subscript. In order to take proper account of intramolecular energy changes, Flory[1] defined λ with respect to an isotropic reference state whose volume V_0 is such that if the real network were compressed to this volume, severance of all the crosslinkages would leave the statistical distribution of the mean-square end-to-end lengths of the network chains unaltered. Using this definition, $\lambda = (L/L_0)$, where L is the deformed length and L_0 is the length of the isotropic sample at volume V_0.

So as to take account of the combination of the chains into a single network, Wall and Flory[8] have argued that a logarithmic term is required in equation (4). It can easily be shown that this additional term has a negligible effect upon the outcome of the present derivation and so for simplicity we have chosen to omit it.

From equations (2), (3) and (4) we obtain

$$\kappa_{L,T}=\kappa_T^* \tag{5}$$

and

$$\gamma_{L,V}=\gamma_V^*-Nk\,V_0^{-2/3}V_i^{-1/3}\alpha^{-1}+Nk\,TV_0^{-2/3}V_i^{-1/3}\alpha^{-1}\mathrm{d}\ln V_0^{2/3}/\mathrm{d}T \tag{6}$$

where† subscript i refers to the sample in the undeformed state at the given T and P and $\alpha=L/L_i$. Adopting the reasoning put forward by Flory we can replace $\mathrm{d}\ln V_0^{2/3}/\mathrm{d}T$ by $\mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T$, where $\overline{r_0^2}$ is the unperturbed mean-square end-to-end distance.

For networks prepared in the absence of diluent we can, to a good approximation, set $V_0=V_i$. Thus from equation (6) we obtain

$$\gamma_{L,V}\simeq\gamma_V^*-Nk\,V_i^{-1}\alpha^{-1}+Nk\,TV_i^{-1}\alpha^{-1}\mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T \tag{7}$$

The last two terms in equation (7) can be ignored since $\gamma_{L,V}$ is of the order of 10 atm.deg^{-1}, $|\mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T|<|1/T|$ and for a lightly crosslinked rubber we can take $Nk\,V_i^{-1}<10^{-2}$ atm.deg^{-1}. Hence we must conclude that a Gaussian network would make a negligible contribution to the normal liquid-like coefficients of expansion and thermal pressure of a rubber.

We must now consider, however, to what extent the behaviour of real systems is likely to differ from the ideal case. Within the narrow range of simple extension where $\beta_{L,P}$, $\kappa_{L,T}$ and $\gamma_{L,V}$ have been measured the elastic properties of real networks are consistent with the empirical Mooney–Rivlin equation

$$f/2(\alpha-\alpha^{-2})=C_1+C_2/\alpha \tag{8}$$

where f is the equilibrium force at elongation ratio α and C_1 and C_2 are elastic constants. The butyl rubber networks investigated in the present study had $C_1=0{\cdot}69$ kg cm^{-2} and $C_2=0{\cdot}25$ kg cm^{-2}, when f is expressed as force per unit undeformed cross-sectional area. Equation (8) is consistent with an elastic free energy expression of the form

$$F_{el}=C_1(\lambda_x^2+\lambda_y^2+\lambda_z^2-3)+C_2(\lambda_x^{-2}+\lambda_y^{-2}+\lambda_z^{-2}-3) \tag{9}$$

Experimental evidence shows that C_1 is, to a first approximation, directly proportional to the absolute temperature and has the same form as the elastic constant in the Gaussian equation of state. The behaviour of C_2 is less well documented, although we shall report elsewhere some experimental evidence that it is also to a first approximation proportional to the absolute temperature, the latter inferring that C_2 as well as C_1 is mainly entropic in origin. Measurements carried out on dry and swollen rubbers

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†Flory's definition[1] of α differs slightly from ours owing to the dilation which occurs on stretching.

suggest that C_2 as defined by equation (9), rather than equation (8), is virtually independent of volume at a given temperature.

Using equation (9) in place of equation (4) and making the assumptions discussed we obtain

$$(\kappa_{L,T})^{-1} \simeq (\kappa_T^*)^{-1} + 2C_2\alpha \tag{10}$$

and

$$\gamma_{L,V} \simeq \gamma_V^* - (2C_1/T)\,\alpha^{-1} + 2C_1\alpha^{-1}\,\mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T + 2C_2\alpha\,\mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T + 2\alpha\,(\partial C_2/\partial T)_{L,V} \tag{11}$$

If we accept that the derivative $\partial C_2/\partial T$ cannot be much greater than C_2/T, which typically will be of the order of 10^{-3} atm.deg^{-1}, then the additional terms appearing in relationships (10) and (11) due to departures from ideality can be neglected. Hence we must conclude that for a lightly crosslinked rubber $\kappa_{L,T} \simeq \kappa_T^*$ and $\gamma_{L,V} \simeq \gamma_V^*$.

It is difficult to explain the results reported for silicone rubber and ethylene-propylene rubber by Bianchi and Pedemonte. However, in the light of our experimental data and agreement with analysis based upon either a Mooney–Rivlin or Gaussian equation of state we conclude that for lightly crosslinked networks, $\kappa_{L,T}$ and $\gamma_{L,V}$ are virtually independent of the extension ratio over the range where it is possible to make equilibrium measurements.

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