Thermoelastic measurements of some elastomers under extension and torsion

Mahmood A. Mohsin* and the late Leslie R. G. Treloar
Department of Polymer Science and Technology, University of Manchester Institute of Science and Technology, Sackville Street, Manchester M60 1QD, UK

(Received 26 March 1987; accepted 18 May 1987)

The relative energetic contribution to the retractive force of a deformed rubber sample, f_e/f, and the corresponding M_e/M have been evaluated from thermoelastic measurements at constant pressure. A wide range of elongations $1.25<\alpha<3.0$ has been studied over the temperature range 20–100°C. Thermoelastic measurements have been obtained for butyl rubber, *cis*-polybutadiene rubber and styrene–butadiene rubber, using two different experimental techniques, the first from measurements of f_e/f in simple extension, and the other from measurements of the internal energy contribution M_e to the restoring couple M in cylindrical rubber samples (subjected to combined torsion about the axis and extension in the axial direction). The results obtained for butyl rubber and styrene–butadiene rubber do not contain any surprising features, and are found to be in good agreement with other reported experimental results for these polymers and their interpretation in terms of rotational isomeric state theory. However, the results for styrene–butadiene did show different trends between two techniques. For *cis*-polybutadiene, on the other hand, the values of f_e/f and M_e/M appear to be substantially dependent on the extension ratio α. The results of this work are used to assess the principal theories of elasticity and it appears that the simple theory based on Gaussian statistics is not universally applicable to all the rubbers at all strains.

(Keywords: thermoelasticity; butyl rubber; *cis*-polybutadiene rubber; styrene–butadiene rubber; stress–temperature coefficient; torsional couple; total stress)

INTRODUCTION

Thermodynamics of rubber in extension

In experiments under the usual (constant-pressure) condition, the internal energy component of the stress arises from two causes: first, the change of volume associated with the hydrostatic component of the tensile stress, and second, the effect of attractive forces between atoms or groups of atoms within the single chain. The first effect can be eliminated by working under constant-volume conditions or (more simply) by correcting the constant-pressure data to equivalent constant-volume data on the basis of Flory's theory[1,2]. Flory's theory starts from the expression for the force–extension relation in simple extension in the form:

$$f=(\nu kT/L_i)(\langle r_i\rangle^2/\langle r_0\rangle^2)(\alpha-\alpha^{-2}) \qquad (1)$$

where f is the tensile force, ν is the total number of chains in the network, k is the Boltzmann constant, $\langle r_i\rangle^2$ is the mean-square end-to-end distance of network chains in the unstrained state, $\langle r_0\rangle^2$ is the unperturbed mean-square length of a corresponding set of chains in the free (i.e. uncrosslinked) state, α is the linear extension ratio ($\alpha=L/L_i$), L_i is the length of the undistorted specimen corresponding to the volume V in the strained state ($L_i=V^{1/3}$) and L is the strained length.

The entropy component of the stress is obtained from the temperature coefficient of the force (f) by differentiation of the above equation at constant volume and constant length. The only quantity in this equation which depends on temperature under these conditions is $\langle r_0\rangle^2$. The results of differentiation with respect to T yields[3]:

$$(\partial\ln(f/T)/\partial T)_{V,L}=-\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T \qquad (2)$$

or

$$(\partial f/\partial T)_{V,L}=(f/T)[1-(T\,\mathrm{d}\ln\langle r_0\rangle^2/dT)] \qquad (3)$$

The energy component of the elastic stress is simply defined from the first law of thermodynamics as follows:

$$f_e=(\partial U/\partial L)_{T,V}=f+T(\partial S/\partial L)_{T,V} \qquad (4)$$

where U is the internal energy and S is the entropy. The entropy and internal energy components of the stress are then obtained from the following equations:

$$(\partial S/\partial L)_{T,V}=-(\partial f/\partial T)_{V,L} \qquad (5)$$

$$f_e=f-T(\partial f/\partial T)_{V,L}=fT\,\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T \qquad (6)$$

The ultimate result is

$$f_e/f=1-(T/f)(\partial f/\partial T)_{V,L}=T\,\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T \qquad (7)$$

Equation (7) was first derived by Flory, Hoeve and Ciferri[3] to express the relative internal energy contribution in terms of the statistical theory. In practice, however, the measurement of $(\partial f/\partial T)_{V,L}$ at constant volume is performed with great difficulty. Flory obtained

---

* Present address: Chemistry Department, University of Stirling, Stirling FK9 4LA, UK

0032-3861/87/111893-06$03.00

a relation between the experimentally more convenient stress–temperature coefficient $(\partial f/\partial T)_{P,L}$ at constant pressure. Equation (1) can be differentiated, this time at constant pressure and length, giving[3]:

$$(\partial \ln(f/T)/\partial T)_{P,L} = -(\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T) - \beta/(\alpha^3-1) \tag{8}$$

From the above equations, the difference between the temperature coefficients of the forces at constant volume and at constant pressure becomes:

$$(\partial \ln(f/T)/\partial T)_{V,L} - (\partial \ln(f/T)/\partial T)_{P,L} = \beta/(\alpha^3-1) \tag{9}$$

where β is the volume expansion coefficient of the rubber, and α is the extension ratio. From equations (6) and (9) the relative energetic component of the force at constant volume is obtained explicitly in the form:

$$f_e/f = 1-(T/f)(\partial f/\partial T)_{P,L} - \beta T/(\alpha^3-1) \tag{10}$$

The temperature coefficients at constant P and at constant α can also be obtained and are given below[3]. For constant pressure P

$$(\partial \ln(f/T)/\mathrm{d}T)_{P,L} = -\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T - \beta/(\alpha^3-1) \tag{11}$$

For constant extension α

$$(\partial \ln(f/T)/\mathrm{d}T)_{P,\alpha} = -\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T + \beta/3 \tag{12}$$

Torsion

The thermodynamic analysis of torsion proceeds on precisely similar lines to that for simple extension[4]. The couple M required to twist a cylindrical sample of length l and radius a_0 through an angle ϕ (torsion $\psi = \phi/l$) is:

$$M = (\pi/2)(\langle r_i\rangle^2/\langle r_0\rangle^2)(\nu kT\psi a_0^4/V_u) \tag{13}$$

where ψ is the torsion (expressed in radians per unit length of the strained axis) and a_0 is the unstrained radius of the sample. The only quantity in this equation which is dependent on temperature is $\langle r_0\rangle$ (if volume, length and twist are kept constant). Differentiation of equation (13) with respect to T at constant volume, length and torsion (P,l,ψ) is thus carried out. For a constant length l, constancy of ϕ is equivalent to constancy of ψ. Therefore

$$\begin{aligned}(\partial M/\partial T)_{V,l,\phi} &= (\partial M/\partial T)_{V,l,\psi} \\ &= (M/T)[1-T(\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T)]\end{aligned} \tag{14}$$

and

$$(\partial M/\partial T)_{P,l,\psi} = (M/T)[1-T\beta - T(\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T)] \tag{15}$$

The relative internal energy contribution to the couple is then obtained in the form:

$$M_e/M = 1-(T/M)(\partial M/\partial T)_{V,l,\phi} \tag{16}$$

From equation (14), substitute the value of $(\partial M/\partial T)_{V,l,\phi}$ in equation (16); then

$$M_e/M = T\,\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T \tag{17}$$

Equation (17) is precisely similar to the corresponding expression for the case of simple extension. In order to obtain the value of M_e/M from an experiment conducted under constant pressure, equations (15) and (17) may be combined to give

$$M_e/M = 1-(T/M)(\partial M/\partial T)_{P,l,\psi} + \beta T \tag{18}$$

The difference between the constant-pressure and constant-volume coefficients is therefore:

$$(\partial M/\partial T)_{P,l,\psi} - (\partial M/\partial T)_{V,l,\psi} = M\beta \tag{19}$$

These conclusions are of considerable interest. Equation (14) illustrates Flory's general conclusion that the temperature dependence of the stress, at constant volume, is directly related to the temperature coefficient of $\langle r_0\rangle^2$. Equations (15) and (19) do indeed confirm Flory's statement in showing that, in the case of torsion, constant-volume and constant-pressure conditions are not equivalent.

There are important quantitative differences between extension and torsion. Whereas in the case of extension the difference between the constant-pressure and constant-volume coefficients tends to infinity at small strains, thus making the measurements extremely sensitive to small variations of unstrained length, in torsion the corresponding difference is independent of strain. The evaluation of M_e/M is therefore not sensitive to the precise measurement of the unstrained dimensions, as is the evaluation of f_e/f.

Gent and Kuan[5] developed a modified form of Treloar's[6] torsional apparatus and employed it to redetermine values of M_e/M for natural rubber, *trans*-isoprene, *cis*-butadiene and high-density polyethylene in both the dry and swollen states. For the first three of these polymers the values of M_e/M were unaffected by swelling, while polyethylene gave an anomalously high (negative) value, which, though decreased by swelling, was still not in accord with the values given in Mark's review[7]. A somewhat disturbing feature of their data was the apparent reduction of M_e/M for the first three polymers with increasing axial strain. In considering these observations, it must be remembered that the equations used to calculate M_e/M are based on the Gaussian network theory. Treloar[8] considered that the observed strain dependence might be attributed to non-Gaussian effects (finite chain extensibility). It could also possibly arise from stress-relaxation effects.

The primary objectives of this work were two-fold, namely:

(a) to repeat the experiments of Gent and Kuan on the effect of axial extension on the relative internal energy contribution to the torsional couple (M_e/M) for different rubbers to see whether their results could be confirmed; and

(b) to carry out comparable simple extension measurements on the same samples to obtain the dependence (if any) of f_e/f on axial strain. Comparison with (a) should be of value in the attempt to find the explanation of the former effect.

EXPERIMENTAL

Materials

Investigations were carried out on three types of elastomeric materials. These were butyl rubber, *cis*-

polybutadiene rubber (containing 98% 1,4-*cis* isomer) and styrene–butadiene rubber (SBR) (containing 23.5% by weight of styrene). All the rubberes were obtained as uncured, unfilled commercial products. (The authors are indebted to the Leyland and Birmingham Rubber Co. Ltd for provision of the styrene–butadiene rubber, to the Hubron Rubber Co. for the *cis*-polybutadiene, and to the Polymer Corporation Ltd, Canada, for the butyl rubber.)

Preparation of samples

Preliminary work has been carried out on all rubbers examined in order to produce a sample which is capable of withstanding the high temperature at higher elongation for a period of time without rupture. Using 0.1% dicumyl peroxide as a crosslinking agent gives a satisfactory test sample for *cis*-polybutadiene and styrene–butadiene rubbers. Following the manufacturer's advice, the butyl rubber was cured with sulphur[9] in the presence of 30% carbon black, and during the experimental test, the sample shows a convincing result. For simple extension experiments parallel-sided specimens were cut to a length of 50 mm and a width of 10 mm from a sheet of cured rubber of 1.0 mm thickness. The test piece for the experiments on torsion was in the form of a cylinder of length 50 mm and diameter 6 mm.

The values of thermal expansion coefficient β for the three rubbers were determined by a dilatometric method over the temperature range 20–100°C. These values together with the compounding formula are included in *Table 1*. The method and the experimental technique for simple extension and torsion were given in detail in previous publications[10,11].

Stress relaxation

Careful consideration was given to the phenomenon of stress relaxation whereby the stress required to maintain a fixed strain decreases with time. Wood and Roth[12] and others[13,14] have suggested that essentially reproducible stress–temperature measurements were obtained if the samples were relaxed at the highest temperature and extension to be used, and that these conditions should never be exceeded subsequently. In accordance with this suggestion, the stretched samples were allowed to relax until the decrease in length or torsional stress became very small and the rate of decrease became less and less. After a sufficient time (6–8 h) the rate becomes small enough to be neglected and the equilibrium state is obtained.

Table 1 Compounding formulae and volume expansion coefficients of rubbers used

Recipe (part by weight)	Butyl rubber	*Cis*-butadiene	SBR
Polymer	100	100	100
Dicumyl peroxide	–	0.1	0.1
Carbon black	30	–	–
Zinc oxide	5	–	–
Steric acid	1	–	–
MBTS[a]	0.5	–	–
TMTD[b]	1	–	–
Sulphur	2	–	–
Cure time (min)	40	15	15
Cure temperature (°C)	150	165	165
Volume expansion coefficient $\times 10^{-4}$ (K^{-1})	4.61	6.90	6.42

[a] Dibenzthiozyl disulphide
[b] Tetramethylthiurame disulphide

RESULTS AND DISCUSSION

Analysis of stress–strain data

The statistical theory of high elasticity predicts a change in internal energy during elongation, linking this change with the transition of one rotary isomer into another as the chain extends. However, with this interpretation of energy, f_e/f values should be independent of the degree of extension. A number of literature data indicated[15–17], however, that f_e/f depends on the degree of extension. It has been shown in some publications[6,18,19] that the experimental error in determining values of f_e/f gradually increases with lower extension. Indeed, from equation (10) it can be seen that the derivation of f_e/f from constant-pressure experiments involves the addition of the term $\beta/(\alpha^3-1)$, which tends to infinity as α tends to unity. A very small error in the measurement of unstrained length, and hence of α, will lead to disproportionately large errors in the derivation of f_e/f at small strains.

In a careful study of this problem Shen[20] demonstrated that the apparent dependence of f_e/f on strain could be eliminated by considering the temperature dependence of the shear modulus G, defined by the equation

$$f = GA_0(\alpha - \alpha^{-2}) \tag{20}$$

where f is the tensile force and A_0 the unstrained area of cross-section. To obtain values of f_e/f he replaced equation (20) by

$$f_e/f = 1 - (\mathrm{d}\ln G/\mathrm{d}\ln T) - (\beta T/3) \tag{21}$$

The shear moduli were not determined directly from measurements of shear, but calculated from tensile elongation data. Therefore, he plotted f against $(\alpha - \alpha^{-2})$ at different temperatures, and he found these plots were linear (within experimental error) and in accordance with equation (20). Since these plots were linear, it follows that f_e/f is independent of strain. The advantage of Shen's equation is that it averages out the experimental error by obtaining the shear moduli. Additionally, the second term on the right-hand side of equation (20) is independent of strain, in contrast to the corresponding term in equation (10). This method has been examined previously for natural rubber[11], and gave values of f_e/f in close agreement with those obtained by direct measurement of the stress–temperature coefficient under constant-volume conditions. The alternative method adopted by Shen and applied in this work involved the measurement of the variation of length with temperature at constant force f (i.e. $\partial l/\partial T)_{f,P}$. This similarly eliminates the need for an accurate measurement of l_0, and also allowed the dependence (if any) of f_e/f on the extension ratio α to be examined over a wide range of elongation.

Analysis of strain–temperature data

Butyl rubber. For butyl rubber the plots of l vs. T at different values of f were linear and reversible in all cases (*Figure 1*). By choosing a particular value of the temperature it was possible to read off values of f and l at constant T. Repetition of this procedure for different values of T then yielded a set of stress vs. length curves for different values of T. These are replotted in *Figure 2*. From these curves, by choosing a particular value of l it was

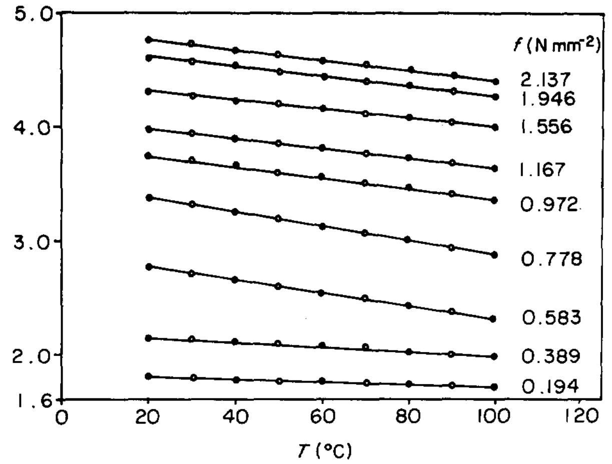

Figure 1 Butyl rubber, variation of length with temperature for different values of the stress: (●) temperature increasing, (○) temperature decreasing

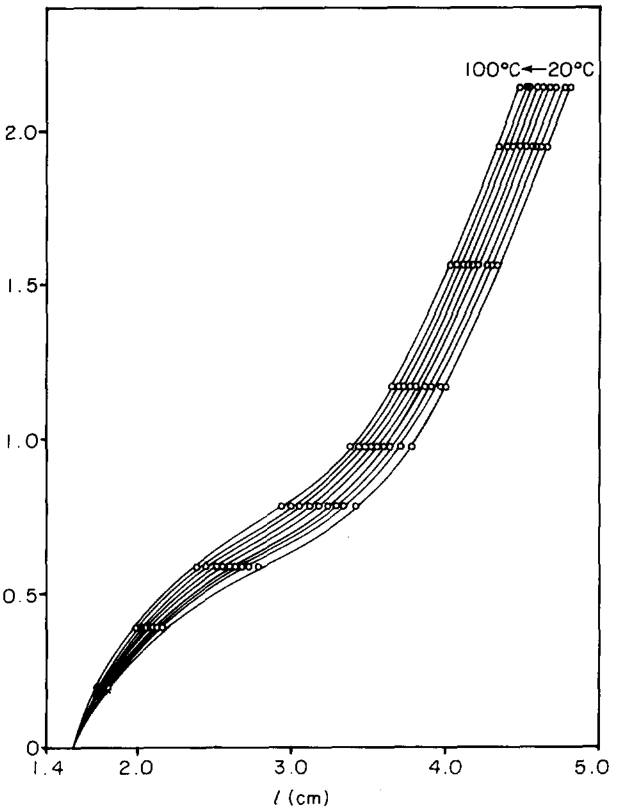

Figure 2 Butyl rubber, stress vs. length for different temperatures, derived from *Figure 1*

equally possible to read off values of f and T at constant l, and these values are plotted in *Figure 3*. The slope of each curve was calculated using a least-squares program and also values of f were calculated at the reference temperature of 20°C. In order to calculate values of α, the initial length l_0 was taken from *Figure 2* at zero stress at the reference temperature. (It is to be noted that since l is constant throughout the stress–temperature curve, the value of $\alpha = l/l_0$ changes slightly with temperature owing to changes in l_0. However, correction for this effect appeared negligible in quantitative treatment and was therefore omitted as suggested by Ciferri *et al.*[21]) A linear dependence of stress on temperature was observed with a positive temperature coefficient of stress $(\partial f/\partial T)_{P,l}$ for all degrees of elongation examined. By using Flory's statistical theory of high elasticity (equation (10)), it was possible to obtain a series of f_e/f values for different extension ratios α. The results of these calculations are reproduced in *Figure 4* (curve A). This indicates that for butyl rubber the values of f_e/f were negative and completely independent of α. This observation is in full accord with the theory of rubber elasticity and it is consistent with the fact that butyl rubber does not crystallize on extension. The mean value of f_e/f obtained in this method was -0.034, which is close to the mean value of -0.03 obtained by Ciferri *et al.*[21] but rather higher than those of -0.08 obtained by Allen *et al.*[19] In all cases the values of f_e/f reported in the literature and in this work were small and negative. The negative values of f_e/f and hence of $\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T$ imply that for this material the intramolecular forces are repulsive.

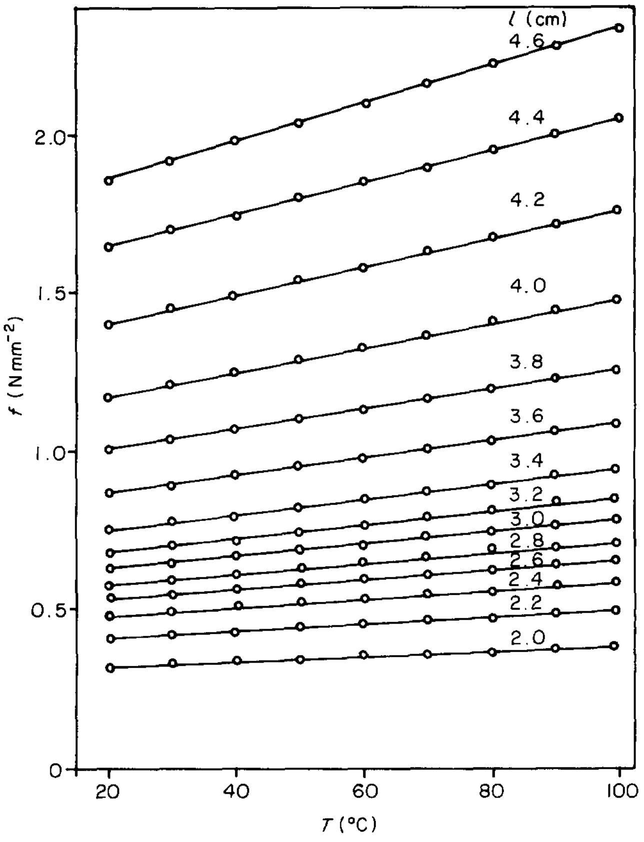

Figure 3 Butyl rubber, stress vs. temperature plots at constant length, derived from *Figure 2*

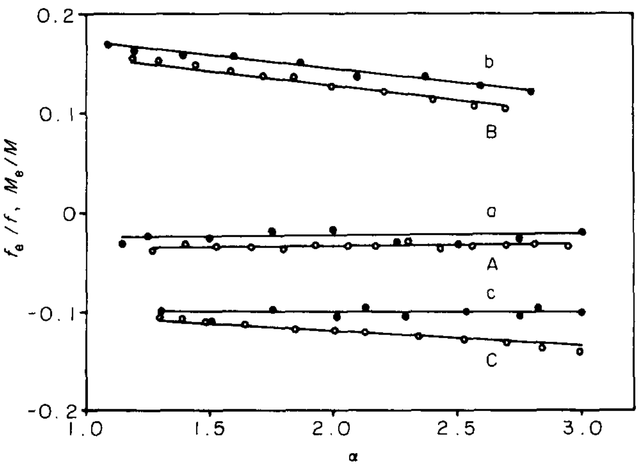

Figure 4 Dependence of f_e/f (○) and M_e/M (●) on extension ratio α. Curves A and a for butyl rubber, curves B and b for *cis*-polybutadiene and curves C and c for styrene–butadiene rubber

Cis-polybutadiene rubber. A similar study based on l vs. T measurements at constant f was carried out on other two rubbers. A substantial decrease in f_e/f with extension has been found for *cis*-polybutadiene rubber (*Figure 4*, curve B). This decreasing tendency is not predicted by the theory of rubber elasticity. The values of f_e/f obtained show that the contribution of energy to the total stress is positive, similar to those obtained previously for natural rubber over the same range of elongations[11].

Styrene-butadiene rubber. The values of f_e/f for this polymer were negative, and slightly strain-dependent, especially at higher values of α as shown in *Figure 4* (curve C). This dependence was unexpected and cannot be attributed to any form of strain-induced crystallization, since this rubber (like butyl rubber) does not crystallize on deformation[11,22]. The average value of f_e/f was -0.115, which is in remarkably good agreement with -0.120 obtained by Cirlin *et al.*[23]

Effect of torsional strain on M_e/M

The second experimental technique used in this work was the torsional method in which a cylindrical rubber sample is extended longitudinally and subjected to torsional stress and strain. A set of stress (torsional couple) vs. temperature data have been plotted in *Figure 5* for butyl rubber at different torsional strains and constant elongation ($\alpha = 2$). In all cases a reversible, linear relationship was found to exist between the couple M and temperature T. Thermodynamic reversibility had been achieved over the total time of the experiment and the whole range of temperature (20–100°C) after mechanical preconditioning for stress relaxation. The slopes of these curves are always positive and analysis of the data shows that the relative slope, and hence the relative internal energy contribution to the couple at constant volume M_e/M, is independent of torsional strain within the range of extensions studied. The torsional strain is expressed in terms of the parameter (ψa_0) depending on the amount of twist in the total length of the sample.

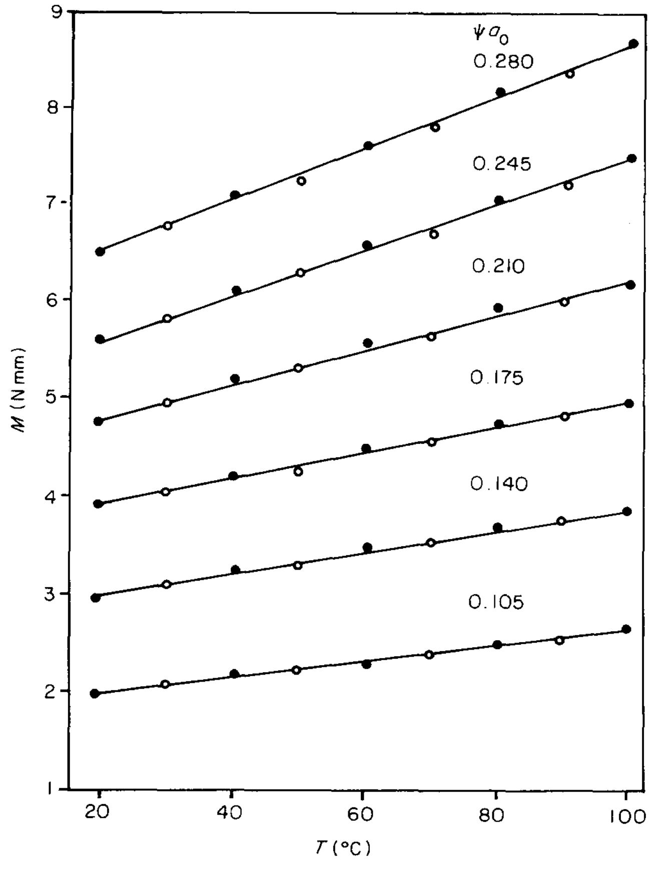

Figure 5 Butyl rubber, stress–temperature relation at constant torsional strain parameter ψa_0 at $\alpha = 2$: (●) temperature increasing, (○) temperature decreasing. Torsional strains are indicated

Analysis of torsion–temperature data

Having established that M_e/M is independent of torsional strain at constant α, the next step was to make measurements over a range of different elongations to establish the variation of M_e/M with α. Thermoelastic curves for butyl rubber at different extension ratios are shown in *Figure 6*. Equilibrium stresses obtained on increasing and decreasing temperature showed complete agreement. Values of M_e/M at each elongation have been calculated from the slope and the value of M at 20°C by means of equation (14). In *Figure 4* (curve a), values of M_e/M were plotted against the extension ratio. It can be seen that M_e/M is consistently independent of α. Similar behaviour of f_e/f with α was observed over the same range of elongations in a simple extension method. The

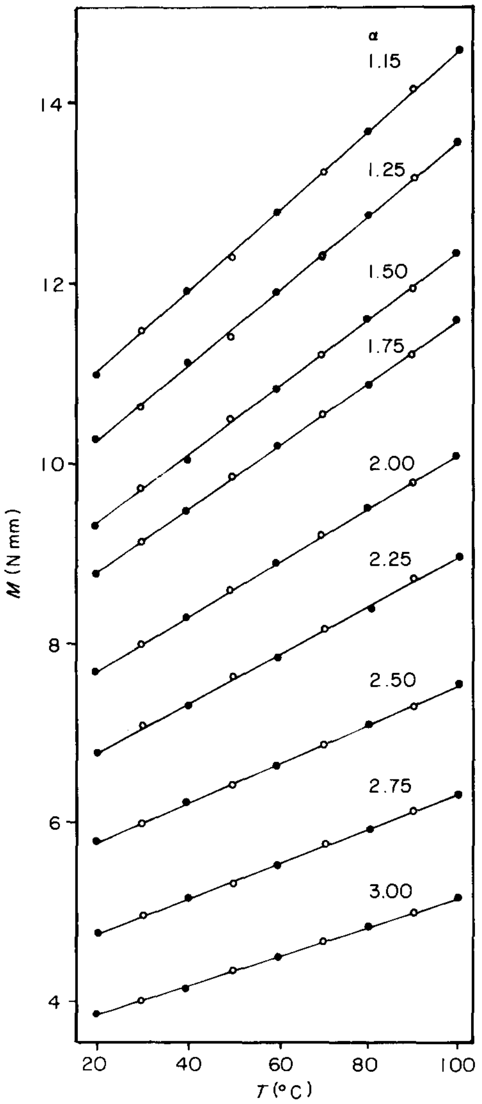

Figure 6 Butyl rubber, stress vs. temperature plots at different values of α: (●) temperature increasing, (○) temperature decreasing

Table 2 Comparison of values of f_e/f and M_e/M

Polymer	Range of α	f_e/f	M_e/M	Average
Butyl rubber	1.25–3.00	-0.034 (± 0.002)	-0.025 (± 0.002)	-0.030
Cis-polybutadiene	1.25–2.80	0.133 (± 0.004)	0.141 (± 0.003)	0.137
Styrene–butadiene	1.30–3.00	-0.115 (± 0.003)	-0.103 (± 0.002)	-0.109

average value of M_e/M is -0.025, which is in good agreement with the corresponding value of f_e/f obtained in this work. The *cis*-polybutadiene (*Figure 4*, curve b), however, showed a continuous linear fall in the value of M_e/M with increasing α, which was in marked contrast to the constancy of M_e/M for butyl rubber and styrene–butadiene rubber. The numerical values of f_e/f and M_e/M for the three rubbers are listed in *Table 2*. A close agreement was found between the two methods, at least in the regions of extension where the values are not changing significantly with strain.

CONCLUSIONS

Values of the relative internal energy contribution to the total elastic force f_e/f and the corresponding values of M_e/M have been evaluated by means of an analysis which assumes the validity of the kinetic theory of rubber elasticity. The results maintain the generally accepted picture that the deformation of the chain is mainly, but not entirely, due to entropy changes, but in addition also involves significant changes in the intramolecular energy. The present values of both f_e/f and M_e/M are generally consistent with previously published data. For some reason, the values of f_e/f for all the rubbers examined are seen to fall consistently below the values of M_e/M and this difference in terms of values is not predicted since both methods of calculation derive from the same theory.

For butyl rubber and *cis*-polybutadiene a remarkably good agreement has been found in terms of numerical values and trends in both experiments. For styrene–butadiene, however, a downward trend was observed with elongation from the simple extension method, while in torsion method values of M_e/M are independent of elongation, and the latter case is in satisfactory agreement with theory. The main conclusion to be drawn from the present work is that the effect of the extension ratio on the value of M_e/M found by Gent and Kuan for *cis*-polybutadiene is broadly confirmed, though the precise form of this variation is not identical in terms of values and trend.

It is important to note that the above results are all based on Gaussian statistical theory, which assumes that all conformations of the chain have the same internal energy. For this case it would follow that $\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T = 0$. There is thus a certain logical restraint in applying this theory to the case when $\mathrm{d}\ln\langle r_0\rangle^2/\mathrm{d}T$ is not zero, which of course implies that internal energy effects occur within the individual chains. Since, according to the above analysis, f_e/f depends only on the temperature dependence of the mean-square length of the free chains $\langle r_0\rangle^2$, it follows that the theory cannot in principle provide any information on the possible dependence of f_e/f on the amount of strain. For this it would be essential to develop a theory which took into account the statistical properties of the network chains in which different energies were associated with different configurations. Such a theory could aim at calculating both the entropy and the internal energy of the chain for all values of the end-to-end distance. On the basis of such a derivation, it would then be possible to calculate the internal energy and entropy terms in the expression for the free energy of the network corresponding to any state of strain or distribution of r values. In the absence of such a detailed theory it does not seem possible to speculate on the way the energetic and entropic components should depend on the amount or type of strain (e.g. tensile, shear, etc.).

REFERENCES

1 Flory, P. J. *Trans. Faraday Soc.* 1961, **57**, 829
2 Flory, P. J. *J. Am. Chem. Soc.* 1956, **78**, 5222
3 Flory, P. J., Ciferri, A. and Hoeve, C. A. J. *J. Polym. Sci.* 1960, **45**, 235
4 Treloar, L. R. G. *Polymer* 1969, **10**, 291
5 Gent, A. N. and Kuan, T. H. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1723
6 Boyce, P. H. and Treloar, L. R. G. *Polymer* 1970, **11**, 21
7 Mark, J. E. *Rubber Chem. Technol.* 1973, **46**, 593
8 Treloar, L. R. G., 'The Physics of Rubber Elasticity', 3rd Edn., Clarendon Press, Oxford, 1975
9 Polymer Corporation Ltd, 'Polymer Handbook', Vol. 2, Sarnia, Canada, 1960
10 Mohsin, M. A., Ph.D. Thesis, UMIST, 1984
11 Mohsin, M. A., Berry, J. P. and Treloar, L. R. G. *Br. Polym. J.* 1986, **18**, 145
12 Wood, L. A. and Roth, F. L. *J. Appl. Phys.* 1944, **15**, 781
13 James, H. M. and Guth, E. *J. Chem. Phys.* 1943, **11**, 455
14 Anthony, R. L., Caston, R. H. and Guth, E. *J. Phys. Chem.* 1942, **46**, 826
15 Crespi, G. and Flisi, U. *Makromol. Chem.* 1963, **60**, 191
16 Roe, R. J. and Krigbaum, W. R. *J. Polym. Sci.* 1962, **61**, 167
17 Wildschut, A. J. *J. Appl. Phys.* 1945, **17**, 51
18 Price, C., Padget, J. C., Kirkham, M. C. and Allen, G. *Polymer* 1969, **10**, 1278
19 Allen, G., Gee, G., Kirkham, M. C., Price, C. and Padget, J. *J. Polym. Sci.* 1968, **C23**, 201
20 Shen, M. *Macromolecules* 1969, **2**, 358
21 Ciferri, A., Hoeve, C. A. J. and Flory, P. J. *J. Am. Chem. Soc.* 1961, **83**, 1015
22 Doherty, W. O. S., Kim, L. L. and Treloar, L. R. G. *Br. Polym. J.* 1980, **12**, 19
23 Cirlin, E. H., Gebhard, H. M. and Shen, M. *J. Macromol. Sci.* 1971, **A5**, 981