The determination of $d\ln\overline{r_0^2}/dT$ by the method of temperature induced creep in tension and torsion

N. G. McCrum
Department of Engineering Science, Oxford University, Parks Road, Oxford, UK
(Received 19 July 1985)

That all conventional thermoelastic experiments on elastomers are founded on an irrational premiss is a striking claim made recently (*Polymer* 1984, **25** (*Commun.*) 213) and one which we now examine in detail using tension as well as torsion techniques. In tension it is shown that κ (the temperature coefficient of $\overline{r_0^2}$) may be obtained from α (the temperature coefficient of J_R^T, the relaxed compliance) which may be determined by performing two step-function experiments. In the first a T- jump is performed at constant force F, $(T-\Delta T)\rightarrow T$, and the extension of the specimen $\Delta l(t)$ observed as a function of time t after the T-jump: in the second a force-jump, $F\rightarrow(F+\Delta F)$, is performed at T, and $\Delta l(t)$ observed as a function of time after the F-jump. The derived quantities $(\Delta l(t)/\Delta T)_F$ and $(\Delta l(t)/\Delta F)_T$ at different values of F are related by,

$$\left(\frac{\Delta l(t)}{\Delta T}\right)_F - l\left(\frac{\beta^\circ}{3}\right) = F\left(\frac{\Delta l(t)}{\Delta F}\right)_T\left(\alpha - \frac{2\beta^\circ}{3}\right)$$

it is thus possible to find α if β°, the temperature coefficient of the volume, is known. Plots of $(\Delta l(t)/\Delta T)_F - l(\beta^\circ/3)$ against $F(\Delta l(t)/\Delta F)_T$ were linear for arbitrary F and arbitrary t. In torsion the analogous equation is

$$\left(\frac{\Delta\theta(t)}{\Delta T}\right)_\Gamma = \Gamma\left(\frac{\Delta\theta(t)}{\Delta\Gamma}\right)_\Gamma(\alpha-\beta^\circ)$$

in which $\Delta\theta(t)$ is the specimen rotation produced at time t after a T-jump or after a torque jump, $\Gamma\rightarrow(\Gamma+\Delta\Gamma)$. Experiments were performed on a copolymer of acrylonitrite and butadiene ($T_g=-7°C$). Linearity was observed between $(\Delta\theta(t)/\Delta T)_\Gamma$ and $\Gamma(\Delta\theta(t)/\Delta\Gamma)_T$. The values of α obtained from tension and torsion agree to within 7%; this error is experimental. It is shown that the conventional analysis due to Shen fails. This failure is due to the use of the Gaussian model and to incorrect treatment of the viscoelastic effects: all existing values of κ and f_e/f in the literature are systematically in error for the same reasons. The magnitude of the error will depend primarily on the temperature, increasing as T approaches the glass transition.

(Keywords: creep; rubber; T-jump; thermoviscoelasticity)

INTRODUCTION

In a recent paper[1] we proposed a new method for measuring κ, the temperature coefficient of the unperturbed mean-square end-to-end vector length of a macromolecule,

$$\kappa = \frac{d\ln\overline{r_0^2}}{dT} \tag{1.1}$$

The method is based on a determination of α, the temperature coefficient of J_R^T, the relaxed shear compliance of the elastomer,

$$\alpha = \frac{d\ln J_R^T}{dT} \tag{1.2}$$

The relationship between α and κ is derived from the theory of rubber elasticity, which gives,

$$J_R^T = \frac{V}{vkT}\frac{\overline{r_0^2}}{\overline{r_i^2}} \tag{1.3}$$

in which $\overline{r_i^2}$ is the mean-square end-to-end vector length of the set of v crosslinked molecules which compose the specimen, which is of volume V at temperature T; k is Boltzmann's constant. Since $\overline{r_i^2}$ is proportional to $V^{2/3}$ it follows that,

$$\kappa = \alpha + \frac{1}{T} - \frac{\beta^\circ}{3} \tag{1.4}$$

in which β° is the temperature coefficient of the volume,

$$\beta^\circ = \frac{d\ln V}{dT} \tag{1.5}$$

0032-3861/86/010047-14$03.00

The new method is based on the premiss that viscoelastic (or hysteresis) effects preclude a determination of J_R^T but that, paradoxically, its temperature coefficient α can be determined very accurately. The new method follows Shen[2], and Wolf and Allen[3] in favouring the creep technique over stress–relaxation, but differs greatly from the procedure used by these authors who follow the traditional time–temperature programme[4] for eliminating viscoelastic effects.

The physical basis of the new experiment is as follows[1]. Consider an elastomer which has been stressed for a long period of time t', say 100 ks, by a constant shear stress σ. Because it is an elastomer, the vast majority of the molecular relaxation processes will have complied with the stress, and the specimen will have deformed by viscoelastic processes to a strain approaching the equilibrium strain, which is σJ_R^T. Note that it is most unlikely that the strain will equal σJ_R^T and, to compound the problem, there is no procedure available to the experimentalist to decide if the strain has attained equilibrium or not. The occurrence of a deviation is due to the fraction—albeit a small fraction—of molecular processes with relaxation times greater than 100 ks. Nevertheless the major fraction of relaxation processes—roughly those with relaxation times below 10 ks—will have deformed completely to equilibrium. The specimen strain when observed over a time of say 0.1 or 1 ks will appear almost stable and little creep will be observable: we term this a state of pseudo-equilibrium. The new determination of α requires two separate experiments, ***both initiated from this state of pseudo-equilibrium.*** In one a small step-function is placed on the temperature and in the other a small step-function is placed on the stress.

The step-functions in temperature and stress are restricted in magnitude so that the generated strain changes are small enough to be governed by the equations of linear viscoelasticity[5]. The step function in stress, $\sigma \rightarrow (\sigma + \Delta\sigma)$, stimulates the specimen to creep, as indicated in *Figure 1*. The state of pseudo-equilibrium is indicated at *a–b*: the time adopted to achieve this, t', is of no quantitative consequence: it has merely to be long enough so that in the forthcoming step-function experiment, the zero at *a–b* is sufficiently stable that the induced deviation from it, $(\Delta\gamma(t))$, can be measured over the experimental timescale (~ 1 ks). The creep increment at time t after the stress-jump, $\Delta\gamma(t)$, is a fraction, $X^T(t)(0 < X^T(t) < 1)$ of $\Delta\gamma_\infty$:

$$\Delta\gamma_\infty = \Delta\sigma J_R^T, \tag{1.6}$$

$$\Delta\gamma(t) = \Delta\gamma_\infty X^T(t) \tag{1.7}$$

$\Delta\gamma(t)$ moves from zero and approaches $\Delta\gamma_\infty$ asymptotically as $X^T(t)$ moves with t from 0 to 1 (*Figure 1*). This stress-jump experiment is conducted isothermally at T.

The companion experiment is one in which a creep strain is generated at the same temperature T by a T-jump. The specimen is brought to pseudo-equilibrium at temperature $(T - \Delta T)$ (*a–b*, *Figure 1*) under stress σ: the stress is maintained at σ and a T-jump, $(T - \Delta T) \rightarrow T$, causes the specimen to commence to creep at T. *The creep strain has the same time dependence as the stress-triggered creep because both creep processes occur at T*: $\Delta\gamma(t)$ is given by equation (1.7) with

$$\Delta\gamma_\infty = \sigma\alpha\Delta T J_R^T \tag{1.8}$$

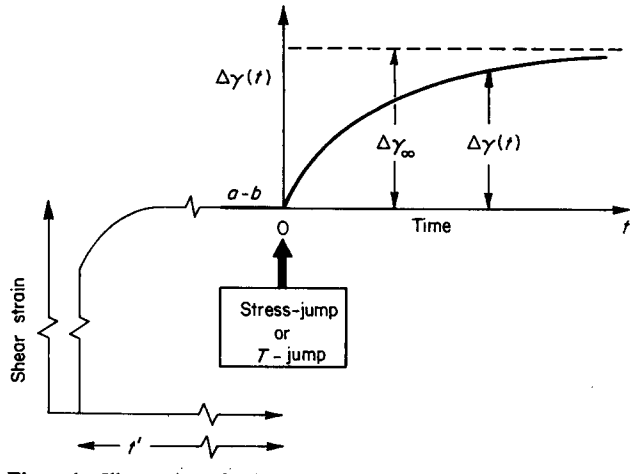

Figure 1 Illustration of a shear creep pulse $\Delta\gamma(t)$ observed over a time 0 to t ($t \sim 1$ ks) and stimulated by a shear stress-jump. The specimen is placed initially under a constant stress σ for a long period of time, t', until the primary creep (at *a–b*) is negligible over the experimental time scale, t: a stress-jump, $\sigma \rightarrow (\sigma + \Delta\sigma)$ then stimulates the secondary creep $\Delta\gamma(t)$ which can be measured precisely without zero-shift when $t \ll t'$: from equations (1.6), (1.7), $\Delta\gamma(t) = X^T(t)\Delta\gamma_\infty$ and $\Delta\gamma_\infty = \Delta\sigma J_R^T$. For a creep pulse $\Delta\gamma(t)$ stimulated by a T-jump, the constant stress σ is placed on the specimen at $(T - \Delta T)$: at time t' a T-jump, $(T - \Delta T) \rightarrow T$, generates $\Delta\gamma(t)$: from equations (1.7), (1.8), $\Delta\gamma(t) = X^T(t)\Delta\gamma_\infty$ and $\Delta\gamma_\infty = \sigma\alpha\Delta T J_R^T$. Since the creep occurs in both experiments at T, $X^T(t)$ and J_R^T are the same thus determining α, equation (1.9)

$\Delta\gamma(t)$ moves asymptotically from zero to $\Delta\gamma_\infty$ as $X^T(t)$ moves from 0 to 1: these results (equations (1.7) and (1.8) hold for $t \ll t'$. It follows from equations (1.6) to (1.8) that if the values of $\Delta\gamma(t)$ are obtained in the two experiments at a *particular value of* t, then the ratio of the two strains is

$$\frac{\sigma\alpha\Delta T J_R^T X^T(t)}{\Delta\sigma J_R^T X^T(t)} = \frac{\sigma\alpha\Delta T}{\Delta\sigma} \tag{1.9}$$

This is the kernel of the experiment stated in its simplest form: the ratio of the observed values of $\Delta\gamma(t)$ in the two experiments conducted at T and assessed at the same time t, yields α. In the experiments the most experimentally convenient values of t lie close to 1 ks: the value of t' is of no significance provided it is much greater than t.

The reader may well ask why, in view of the voluminous literature concerned with this vital topic and the considerable variety of experimental methods which have been adopted[6,7], yet another should be proposed. The answer is that the earlier methods, different although they may be in matters of detail, are all based on a false elimination of the viscoelastic perturbation. There is another source of error also, the use of the equation of the ideal Gaussian chain, which is a traditional source of debate and which we will be required to tackle in this paper. But the overriding error in all earlier work is the elimination of the viscoelastic perturbation by the use of an experimental programme based on what may be called an exhaustion model[1]. In this, the specimen is deformed for a long time at the highest temperature to be used until such time as the creep rate is 'sensibly negligible'. It is then cooled and measurements taken, the assumption being that equilibrium has been achieved at this highest temperature and viscoelastic effects thereby exhausted; the specimen is then presumed to pass through equilibrium states and yield equilibrium data at the lower temperatures.

In summary the traditional experimental analysis contains three errors:

(1) Equilibrium is not attained initially at the highest temperature.

(2) Equilibrium is not attained at lower temperatures on the cooling and heating cycle.

(3) The Gaussian network theory does not hold for all elastomers, and may not hold for any to within the required precision.

Of these it is probably (2) which is the most systematically formidable, since errors (1) and (3) may, in particular instances, not lead to substantial inaccuracy: unfortunately there is no measure of what this inaccuracy may be. A major virtue of the new method is that the procedure remains valid in the unlikely event that the specimen attains equilibrium at all temperatures: that is, the method is fail-safe and is rational and precise whether or not equilibrium is attained.

In this paper we extend the new method from shear to tension. It seemed correct to establish the technique in both shear and in tension and to compare the values of α obtained by the two methods. This provides a particularly rigorous and exacting test of the theory and experimental procedures. Opportunity was taken to improve the precision of the shear method by improvements to the apparatus and by changing the experimental conditions: this meant increasing the value of $\Delta\gamma$ by doubling the value of ΔT, making many repeat experiments using the same ΔT at different values of shear stress, and by doubling the value of t (from 0.6 to 1.2 ks) at which the two values of $\Delta\gamma(t)$ are recorded. It also seemed correct to reformulate the theory so that both shear and tension could be rendered within a single framework and this is presented in the following section. The major part of the work concerns the tension method since this is a simpler experiment—the observable effects in torsion are considerably smaller—and because, although this was not part of our programme, κ and f_e/f can be determined over a range of extension ratios.

THEORY

We examine the effect of viscoelastic creep on the interpretation of a thermo-elastic experiment both in torsion and in tension. In both experiments it is not possible when changing the temperature to keep the stress constant since the dimensions change unavoidably and at constant torque (or force) the stress changes unavoidably. This will necessitate a slightly more complex treatment than the simpler constant stress constraint which led to equation (1.9). Only experiments at constant (atmospheric) pressure are discussed so all differentials will be made with the pressure held constant.

Torsion

Consider a thin walled tube of radius r, wall thickness s and length l twisted by a constant torque Γ around its axis. A thin-walled tube is not the favoured geometry for experimental reasons, but as a model for the theory it yields an essential insight. *If the tube is elastic* and of compliance J then the relationship between the describing parameters, θ the angle of twist of one end with respect to the other, the shear strain in the tube γ, and the shear stress σ generating the rotation is

$$\theta=\left(\frac{l}{r}\right)\gamma=\left(\frac{l}{r}\right)\sigma J \tag{2.1}$$

The shear stress is,

$$\sigma=\frac{\Gamma}{2\pi r^2 s} \tag{2.2}$$

so that

$$\theta=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)J \tag{2.3}$$

The specimen responds elastically to the stress σ: we examine the effect of a small step-function change in σ which is developed (see equation (2.2)) by (i) pulsing the torque from Γ to $(\Gamma+\Delta\Gamma)$ or by (ii) pulsing $(r^2 s)$ from $(r^2 s)$ to $[(r^2 s)+\Delta(r^2 s)]$. The latter step-function is generated unavoidably when the temperature is pulsed, $(T-\Delta T)\rightarrow T$. If the tube is isotropic and of volume thermal expansion coefficient β°, then

$$\Delta(r^2 s)=(r^2 s)\beta^\circ\Delta T \tag{2.4}$$

Note that for an isotropic material (l/r), equation (2.3), does not change when the temperature is pulsed. If both $\Delta\Gamma$ and ΔT are imposed simultaneously then, from equations (2.2) and (2.4),

$$\frac{\Delta\sigma}{\sigma}=\frac{\Delta\Gamma}{\Gamma}-\frac{\Delta(r^2 s)}{r^2 s}=\frac{\Delta\Gamma}{\Gamma}-\beta^\circ\Delta T \tag{2.5}$$

It then follows from equations (2.1) and (2.5) that, the step-function in θ, $\Delta\theta$, produced by the pair of small step-functions $\Delta\Gamma$ and ΔT, is

$$\Delta\theta=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)\left[\frac{\Delta\Gamma}{\Gamma}-\beta^\circ\Delta T\right]J \tag{2.6}$$

So far we have assumed that the change in temperature $(T-\Delta T)\rightarrow T$ produces no change in elastic compliance J. If J does depend on temperature and if the temperature coefficient is α, then reformulation of equation (2.6) shows that

$$\Delta\theta=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)\left[\frac{\Delta\Gamma}{\Gamma}-\beta^\circ\Delta T+\alpha\Delta T\right]J \tag{2.7}$$

In the normal thermoelastic experiment a step function is imposed on the temperature at constant Γ in which case,

$$\left(\frac{\Delta\theta}{\Delta T}\right)_\Gamma=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)[\alpha-\beta^\circ]J \tag{2.8}$$

The other observable is the $\Delta\Gamma$ induced change $\Delta\theta$ at constant T, which, from equation (2.7), is

$$\left(\frac{\Delta\theta}{\Delta\Gamma}\right)_T=\left(\frac{l}{r}\right)\left(\frac{1}{2\pi r^2 s}\right)J \tag{2.9}$$

It then follows from equation (2.8) and (2.9) that,

$$\left(\frac{\Delta\theta}{\Delta T}\right)_\Gamma=\Gamma\left(\frac{\Delta\theta}{\Delta\Gamma}\right)_T[\alpha-\beta^\circ] \tag{2.10}$$

A plot of $(\Delta\theta/\Delta T)_\Gamma$ against $\Gamma(\Delta\theta/\Delta\Gamma)_T$ derived from experiments at different values of Γ should yield a straight line of slope $[\alpha-\beta^\circ]$. If β° is determined, or otherwise known, then α is determined.

We now determine the relevance of equation (2.10) to a thin-walled elastomeric tube which is *linearly viscoelastic*: we will show that the equation holds provided $(\Delta\theta/\Delta T)_\Gamma$ and $(\Delta\theta/\Delta\Gamma)_T$ are determined at the *same time* after the torque-jump and T-jump. If a constant torque Γ is applied at $t=0$ the shear stress (equation (2.2)) generates a rotation and shear strain which depend on t, the time after the imposition of Γ; instead of equations (2.1) and (2.3) we have,

$$\theta(t)=\left(\frac{l}{r}\right)\gamma(t)=\left(\frac{l}{r}\right)\sigma J^T(t) \tag{2.11}$$

$$=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)J^T(t) \tag{2.12}$$

For a linear viscoelastic solid the creep shear compliance is[5],

$$J^T(t)=J_U^T+(J_R^T-J_U^T)X^T(t) \tag{2.13}$$

J_U^T and J_R^T are the unrelaxed and relaxed compliances,

$$X^T(t)=\int_{-\infty}^{\infty}\Phi^T(\ln\tau)(1-\exp(-t/\tau))\mathrm{d}\ln\tau \tag{2.14}$$

$\Phi^T(\ln\tau)$ is the distribution of relaxation times[5]. Equation (2.13) can be simplified for an elastomer (for which $J_R/J_U\sim 10^3$) by neglecting J_U^T in comparison with J_R^T, so that,

$$J^T(t)=J_R^T X^T(t) \tag{2.15}$$

This equation holds for all values of t accessible in step function experiments which, in practice, certainly means for all values of t greater than approximately 1 ms. $X^T(t)$ takes values,

$$0\leqslant X^T(t)\leqslant 1$$

when $X^T(t)=1$ (for $t=\infty$) the compliance observed in the creep experiment yields J_R^T, the relaxed compliance of the elastomer.

To illustrate the argument we consider the temperature induced changes in σ and J_R^T separately. Consider first a specimen with J_R independent of temperature ($\alpha=0$) but with a finite thermal expansion coefficient β°. Assume that it has been stressed for an infinite time (we later relax this constraint) by torque Γ so that from equation (2.11),

$$\theta_\infty=\left(\frac{l}{r}\right)\sigma J_R \tag{2.16}$$

From this equilibrium state if a step function is placed on the stress, σ to $(\sigma+\Delta\sigma)$, the specimen begins to creep again. The stress jump may be generated by a torque-jump, $\Delta\Gamma$, or by a temperature jump, ΔT. If the $\Delta\Gamma$ and ΔT-jumps are imposed at the same time ($t=0$), the rotation produced by the consequent stress-jump is at time t later,

$$\Delta\theta(t)=\left(\frac{l}{r}\right)\Delta\sigma J(t) \tag{2.17}$$

$$=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)\left[\frac{\Delta\Gamma}{\Gamma}-\beta^\circ\Delta T\right]J_R X^T(t) \tag{2.18}$$

This is the time dependent creep occurring at T produced by a temperature jump ΔT, $(T-\Delta T)\rightarrow T$ and by a simultaneous torque jump of $\Delta\Gamma$.

We now relax the constraint of a temperature independent J_R. The T-jump induces a change from $J_R^{T-\Delta T}$ to J_R^T and this is of magnitude for small ΔT, $\alpha\Delta T J_R^T$. The viscoelastic elements are in equilibrium with the stress at $(T-\Delta T)$: following the T-jump to T they are no longer in equilibrium and they commence to move from one equilibrium strain ($\sigma J_R^{T-\Delta T}$) to the other (σJ_R^T). They do this, of course, at temperature $T$by the creep process. This adds another term to the creep at Tyielding (see equations (2.7) and (2.18)),

$$\Delta\theta(t)=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)\left[\frac{\Delta\Gamma}{\Gamma}-\beta^\circ\Delta T+\alpha\Delta T\right]J_R^T X^T(t) \tag{2.19}$$

Two experiments are required to determine α. In the first, a T-jump is imposed, $(T-\Delta T)\rightarrow T$, at constant torque and from equation (2.19) this yields,

$$\left(\frac{\Delta\theta(t)}{\Delta T}\right)_\Gamma=\left(\frac{l}{r}\right)\left(\frac{\Gamma}{2\pi r^2 s}\right)[\alpha-\beta^\circ]J_R^T X^T(t) \tag{2.20}$$

In the second, a Γ-jump is imposed isothermally at T and from equation (2.19) this yields,

$$\left(\frac{\Delta\theta(t)}{\Delta\Gamma}\right)_T=\left(\frac{l}{r}\right)\left(\frac{1}{2\pi r^2 s}\right)J_R^T X^T(t) \tag{2.21}$$

It follows from equations (2.20) and (2.21) that,

$$\left(\frac{\Delta\theta(t)}{\Delta T}\right)_\Gamma=\Gamma\left(\frac{\Delta\theta(t)}{\Delta\Gamma}\right)_T[\alpha-\beta^\circ] \tag{2.22}$$

The reader will recall that this attractive equation has been derived for a linear viscoelastic specimen which has been stressed to equilibrium ($t'=\infty$) before the imposition of the step-functions (ΔT or $\Delta\Gamma$). We now argue that equation (2.22) holds also for $t'\gg t$, t being the time after the step-function over which $\Delta\theta(t)$ is observed.

When observations are taken over a time t (say, $0<t<1$ ks), then the viscoelastic processes under observation are those in the range 0 to 10 ks. If the stress is applied for a time $t'\gg t$, then these short relaxation times will be in equilibrium. The specimen may not be in equilibrium as a whole, *but the relaxation times to be probed in the step-function experiments will be in equilibrium.* It follows that the response to step-functions, either ΔT or $\Delta\Gamma$, will be independent of t': that is, the response when $t'\gg t$ will be the same as when $t'=\infty$. This statement is based on the Boltzmann superposition principle. In which case equation (2.22), derived for $t'=\infty$, holds also for $t'\gg t$. This point is easily checked during the experiment: the experimentalist can measure the $\Delta\theta(t)$ response to successive jumps in ΔT and $\Delta\Gamma$ (at increasing values of t') and determine whether or not the response has become independent of t'.

The specific experimental schedule is as follows.

(i) A state of pseudo-equilibrium is set up at $(T-\Delta T)$ by applying a torque Γ for a time t'.

(ii) A T-jump is imposed, $(T-\Delta T)\rightarrow T$, and the time dependence of $\Delta\theta$ observed up to a time $t(t\ll t')$ after the T-jump (*Figure 1*).

(iii) After the specimen has been at T for a sufficient time to stabilize, a torque jump is imposed, $\Gamma \rightarrow (\Gamma + \Delta\Gamma)$ and the time dependence of $\Delta\theta$ observed up to a time t (the same value as in (ii)). Following a series of such experiments at different values of Γ, for specific values of t, a series of points is plotted $(\Delta\theta(t)/\Delta T)_\Gamma$ against $\Gamma(\Delta\theta(t)/\Delta\Gamma)_T$: these points for the different values of Γ and any value of t should lie on a line of slope $(\alpha - \beta^\circ)$. Hence α is determined if β° is known.

The reader will note that it is to develop physical insight and for ease and economy of presentation that we have set up equation (2.19) showing the result of simultaneous torque and temperature jumps on the rotation: in the experiments this is not done, a step-function being imposed on T (at constant torque) *or* on Γ (at constant temperature).

Tension

For an elastomer, tension is an intrinsically non-linear form of deformation and is on this account more complex to analyse than shear. For torsion we have restrained the treatment to linear deformation as the response to both the major stress σ and to the smaller step-function $\Delta\sigma$ (induced by both temperature and torque jump). We now consider the effect of small temperature and load jumps on the tensile elongation of an elastomer.

If a strip of elastomer of length l_0 and cross-sectional area A_0 is subjected to a force F at temperature T, then according to the Gaussian network theory, the nominal stress σ is related to ratio of the instantaneous length l to the initial length l_0,

$$\lambda = \frac{l}{l_0}$$

by,

$$\sigma = \frac{F}{A_0} = G_R^T f(\lambda) \tag{2.23}$$

in which G_R^T is the relaxed shear modulus,

$$G_R^T = 1/J_R^T \tag{2.24}$$

and $f(\lambda)$ is given[4,7],

$$r(\lambda) = (\lambda - 1/\lambda^2) \tag{2.25}$$

The earlier thermoelastic work is perturbed by two problems[4,6,7]. First, it is by no means certain that $f(\lambda)$ is given sufficiently precisely and for all elastomers by equation (2.25). Second, it is certain that all elastomers are viscoelastic to a greater or lesser extent. We tackle these two problems in succession.

In order to aid the development of the theory assume first that there are no viscoelastic effects, that the imposition of a constant force F generates an extension ratio λ which is independent of time and is related to σ by equation (2.23), and that $f(\lambda)$ is a function of λ which may, or may not be given by equation (2.25). If a temperature jump of ΔT is imposed at constant F, it follows from equation (2.23), after taking logs and differentiating that,

$$-\beta_A^\circ = -\alpha + \frac{f'(\lambda)}{f(\lambda)}\left[\frac{1}{l_0}\frac{dl}{dT} - \frac{l}{l_0^2}\frac{dl_0}{dT}\right] \tag{2.26}$$

where,

$$f'(\lambda) = \frac{df(\lambda)}{d\lambda}$$

and in which β_A° is the temperature coefficient of the cross-sectional area A_0, equal to $(2/3)\beta^\circ$ for an isotropic elastomer. It follows from equation (2.26), that since $\lambda = l/l_0$,

$$(\alpha - \beta_A^\circ) = \frac{f'(\lambda)}{f(\lambda)}\lambda[\beta_L^F - \beta_L^\circ] \tag{2.27}$$

in which β_L° is the temperature coefficient of the unstressed length l_0, equal to $(1/3)\beta^\circ$ for an isotropic elastomer: β_L^F is the temperature coefficient of length under constant force F. In order to proceed we require the term $\lambda f'(\lambda)/f(\lambda)$. If $f(\lambda)$ is given by equation (2.25) then,

$$\frac{\lambda f'(\lambda)}{f(\lambda)} = \left[\frac{\lambda^3 + 2}{\lambda^3 - 1}\right]$$

so that,

$$(\alpha - \beta_A^\circ) = \left[\frac{\lambda^2 + 2}{\lambda^3 - 1}\right](\beta_L^F - \beta_L^\circ) \tag{2.28}$$

This equation* was derived and first used by Shen[2]. We reject it for two reasons: first it is based on equation (2.25) the applicability of which is under attack: second, because it assumes an elastic model with no time effects.

It is fortunate that these simplifying, conventional and erroneous assumptions may be avoided by a direct and precise determination of the quantity $[\lambda f'(\lambda)/f(\lambda)]$, although $f(\lambda)$ itself cannot be determined so easily. From equation (2.23) the functions $f(\lambda)$ and $f'(\lambda)$ are,

$$f(\lambda) = \frac{F}{A_0 G_R^T} \tag{2.29}$$

$$f'(\lambda) = \frac{1}{A_0 G_R^T}\left(\frac{\Delta F}{\Delta\lambda}\right)_T \tag{2.30}$$

The form of this equation anticipates its experimental adaptation in writing $(\Delta F/\Delta\lambda)_T$ instead of $(dF/d\lambda)_T$. In the experiment small step-function changes are made, $F \rightarrow (F + \Delta F)$ and $(T - \Delta T) \rightarrow T$. The magnitude of the ΔF etc. imposed, is sufficiently small to ensure the accuracy of the method, which is based on $(\Delta F/\Delta\lambda)_T \equiv (dF/d\lambda)_T$ etc. It follows from equations (2.29) and (2.30) that,

$$\lambda\frac{f'(\lambda)}{f(\lambda)} = \frac{\lambda}{F}\left(\frac{\Delta F}{\Delta\lambda}\right)_T \tag{2.31}$$

Substituting this in equation (2.27) yields,

$$\alpha - \beta_A^\circ = \frac{\lambda}{F}\left(\frac{\Delta F}{\Delta\lambda}\right)_T [\beta_L^F - \beta_L^\circ] \tag{2.32}$$

* Equation 15 of ref. 2 is erroneous: β_A° is equated with $2\beta_L^\circ/3$.

Since $\lambda = l/l_0$,

$$\left(\frac{\Delta F}{\Delta \lambda}\right)_T = l_0\left(\frac{\Delta F}{\Delta l}\right)_T \tag{2.33}$$

so that,

$$l(\beta_L^F - \beta_L^\circ) = F\left(\frac{\Delta l}{\Delta F}\right)_T (\alpha - \beta_A^\circ) \tag{2.34}$$

which yields by definition of β_L^F,

$$\left(\frac{\Delta l}{\Delta T}\right)_F - l\beta_L^\circ = F\left(\frac{\Delta l}{\Delta F}\right)_T (\alpha - \beta_A^\circ) \tag{2.35}$$

Thus a plot of $(\Delta l/\Delta T)_F - l\beta_L^\circ$ against $F(\Delta l/\Delta F)_T$ should yield a straight line, passing through the origin and of slope $(\alpha - \beta_A^\circ)$.

We turn now to examine the effect of viscoelastic creep. Let the specimen be loaded by force F and let it creep for a long period of time t'. It will not be supposed that the equilibrium condition given by equation (2.23) is reached but that for short experimental times t, during which the specimen is to be perturbed by small step functions ΔT or ΔF, the change in length due to the primary creep imposed by the major force F is negligible. We will assume that under this condition the response of the specimen to small step-functions, ΔF or ΔT, is linearly viscoelastic: this point can be easily checked, and will be so checked in the experimental programme. Suppose that an F-jump, $F \rightarrow (F + \Delta F)$ is imposed: this generates a jump in the stress and therefore a time dependent increment in the strain given,

$$\Delta\varepsilon(t) = \Delta\sigma D^\lambda(t) \tag{2.36}$$

$D^\lambda(t)$ is the tensile creep compliance relevant to the particular extension ratio λ at which the experiment occurs: λ depends on F and to a lesser extent on t', the time permitted for primary creep: $D^\lambda(t)$ depends on λ and relates the stress increment $\Delta\sigma = \Delta F/A_0$ to the strain increment,

$$\Delta\varepsilon(t) = \frac{\Delta l(t)}{l_0} \tag{2.37}$$

Note that $\Delta\sigma$ and $\Delta\varepsilon(t)$ are referred to the unstressed dimensions A_0 and l_0. $D^\lambda(t)$ may be measured by establishing pseudo-equilibrium at λ and then performing isochronal experiments: for example by stressing by force F for $t' = 100$ ks and then measuring for $t = 100$ s values of $\Delta\varepsilon(t)$ for several different values of ΔF. Such experiments are described below both to establish the validity of equation (2.36) (that is, to establish that for small ΔF the specimens obey the equations of linear viscoelasticity) and to use the observed value of $D^\lambda(t)$ in the interpretation of the viscoelastic experiment.

When a small F-jump ($\Delta F \ll F$) is imposed simultaneously with a small T-jump the stress-jump is $\Delta\sigma$,

$$\frac{\Delta\sigma}{\sigma} = \frac{\Delta F}{F} - \frac{\Delta A_0}{A_0}$$

The time dependent strain generated by $\Delta\sigma$ is from equation (2.36),

$$\Delta\varepsilon(t) = \Delta\sigma D_R^\lambda X_\lambda^T(t) \tag{2.38}$$

$X_\lambda^T(t)$ is the relevant tension parameter, analogous to $X^T(t)$ for shear: note that, as in the neglect of the unrelaxed shear compliance in the torsion theory, we have neglected the unrelaxed tensile compliance. The fractional change in A_0 is induced by the T-jump is $\beta_A^\circ \Delta T$, so that

$$\Delta\varepsilon(t) = \sigma\left[\frac{\Delta F}{F} - \beta_A^\circ \Delta T\right] D_R^\lambda X_\lambda^T(t) \tag{2.39}$$

D_R^λ is obtained from equation (2.23) in the following way.

Note that equation (2.23) relates the equilibrium or relaxed parameters σ and λ to the relaxed shear modulus. Differentiating equation (2.23) at constant temperature with respect to λ yields,

$$\frac{d\sigma}{d\lambda} = G_R^T f'(\lambda) \tag{2.40}$$

Noting that $d\lambda = d\varepsilon$ and that at equilibrium,

$$\frac{d\varepsilon}{d\sigma} = D_R^\lambda$$

we have,

$$D_R^\lambda = \frac{J_R^T}{f'(\lambda)}$$

in which we have used $J_R^T = 1/G_R^T$. It then follows from equation (2.39), that the time dependent strain pulse $\Delta\varepsilon(t)$ produced by a stress-jump (generated by a simultaneous F and T-jump) is,

$$\Delta\varepsilon(t) = \sigma\left[\frac{\Delta F}{F} - \beta_A^\circ \Delta T\right]\frac{J_R^T}{f'(\lambda)} X_\lambda^T(t) \tag{2.41}$$

The T-jump will also produce a step-change in J_R and this, by analogy with equation (2.19), will yield a total time dependent pulse in strain,

$$\Delta\varepsilon(t) = \sigma\left[\frac{\Delta F}{F} - \beta_A^\circ \Delta T + \alpha\Delta T\right]\frac{J_R^T}{f'(\lambda)} X_\lambda^T(t) \tag{2.42}$$

The two required experiments are the T-jump at constant F and the F-jump at constant T. The first is interpreted from equation (2.42),

$$\left(\frac{\Delta\varepsilon(t)}{\Delta T}\right)_F = \sigma[\alpha - \beta_A^\circ]\left(\frac{J_R^T}{f'(\lambda)}\right) X_\lambda^T(t) \tag{2.43}$$

The second experiment is from equation (2.42),

$$\left(\frac{\Delta\varepsilon(t)}{\Delta F}\right)_T = \frac{\sigma}{F}\left(\frac{J_R^T}{f'(\lambda)}\right) X_\lambda^T(t) \tag{2.44}$$

It follows using equation (2.37) that,

$$\left(\frac{\Delta l(t)}{\Delta T}\right)_F = F\left(\frac{\Delta l(t)}{\Delta F}\right)_T (\alpha - \beta_A^\circ)$$

Note that the normal expansion change in length has not been taken into account: this will occur instantaneously at the T-jump (no time effect) and be of magnitude $l\beta_L^\circ$ per

°C. It follows then, that at time t after the T-jump, the total change in length $\Delta l(t)$ per °C due to all causes is,

$$\left(\frac{\Delta l(t)}{\Delta T}\right)_F = l\beta_L^\circ + F\left(\frac{\Delta l(t)}{\Delta F}\right)_T (\alpha - \beta_A^\circ) \qquad (2.45)$$

The adopted experimental analysis is a plot of $(\Delta l(t)/\Delta T)_F - l\beta_L^\circ$ *versus* $F(\Delta l(t)/\Delta F)_T$.

The use of equation (2.45) in deriving α is as follows.

(i) At $(T-\Delta T)$ a state of pseudo-equilibrium is established under tensile force F and then, following a T-jump $(T-\Delta T)\downarrow T$, the time dependence of Δl is observed.

(ii) After the creep rate at T following the T-jump has become vanishingly small (of order of the noise in the observations) a force-jump ΔF is imposed and the time dependence of Δl observed.

Following a series of such experiments at different values of F, for specific values of t, a series of points is plotted $(\Delta l(t)/\Delta T)_F - l\beta_L^\circ$ against $F(\Delta l(t)/\Delta F)_T$: these points, for the different values of F and for arbitrary value of t ($t \ll t'$), should lie on a line of slope $(\alpha - \frac{2}{3}\beta^\circ)$. Hence α is determined: β_L° is determined from the observed $(\Delta l/\Delta T)$ at $F=0$ and yields $\beta^\circ (= 3\beta_L^\circ)$.

EXPERIMENTAL

The experiments were performed on a crosslinked copolymer of acrylonitrile and butadiene ($T_g = -7$°C). The principal requirement was for an elastomer insensitive to to moisture with a T_g in an experimentally convenient temperature region and with excellent thermal stability and good mechanical strength. This polymer was used in earlier studies and its preparation is described elsewhere[8]. It was obtained as a compression moulded sheet from which specimens for the shear and tensile experiments were cut. The torsion experiment was performed on a blade shaped specimen because (i) it could be cut from the identical sheet from which the tension specimen was cut: (ii) a thin-walled tube is unstable (it buckles) when twisted through other than very small values of (θ/l).

The requirements of the experiment are to hold the specimen under constant temperature and force (or torque) with a facility to impose a step-function in either temperature or force (or torque). Our adaptation of the essentially standard procedures by which this may be done for torque and force will be outlined. For the step-function in temperature there is no doubt that the sharpest and most precise T-jumps are to be obtained with a flowing liquid in direct contact with the specimen: although highly successful with the right polymer (for example, polypropylene in water[9], temperature range 20°C to 60°C), the liquid method is inflexible since in general liquid absorption will occur, or the desired temperature range is unattainable, or the flowing liquid stimulates vibration in a low modulus specimen—such as an elastomer. We turned therefore to flowing gas: the T-jump is not so sharp as is obtainable with liquid. The perturbation caused by the unsharp T-jump may be eliminated however, by taking the observation time t sufficiently long that the results are independent of t. For example, suppose the ramp time from $(T-\Delta T)\downarrow T$ is one minute (which is about the observed value). But after, it will be shown, 15 min the rate of creep is sufficiently low that the one minute ramp time can be neglected: the data points for $t = 15$, 20, 25, 30 min fall on a line given by equation (2.45). This result was anticipated: an example of the evidence is shown in *Figure 6*.

Tensile experiment

The specimen, A, was mounted between a fixed lower clamp, B, and the upper clamp, C, which was at the end of a pull-rod, D, *Figure 2*. The apparatus was made of Invar. The force F in the pull-rod was generated by a mass placed in pans 1 and 2, with mechanical advantages 1.0 and 2.0 as indicated. The mass in pan 1, exactly counterbalanced the system, so that when there was zero mass in pan 2 the force F in the pull-rod was negligible. In order to develop a state of pseudo-equilibrium a mass $M/2$ was placed in pan 2 generating a force $F = Mg$ in the pull-rod: under this force the specimen commenced to creep. The length change of the specimen was observed by the movement of the core E through the barrel of an LVDT, G. The barrel was held firmly by a collar H attached to a micrometer: rotation of the micrometer permitted movement of the collar and barrel vertically. The output voltage of the LVDT was measured on a chart recorder: for most observations a 1.0 mm movement of the core within the barrel was represented by a 288 mm deflection of the pen of the recorder (working on a scale 100 mV equals 200 mm deflection of the recorder). The calibration of the system was checked daily; the barrel and collar were moved using the micrometer with the core stationary. A core/barrel displacement of known magnitude was thus generated.

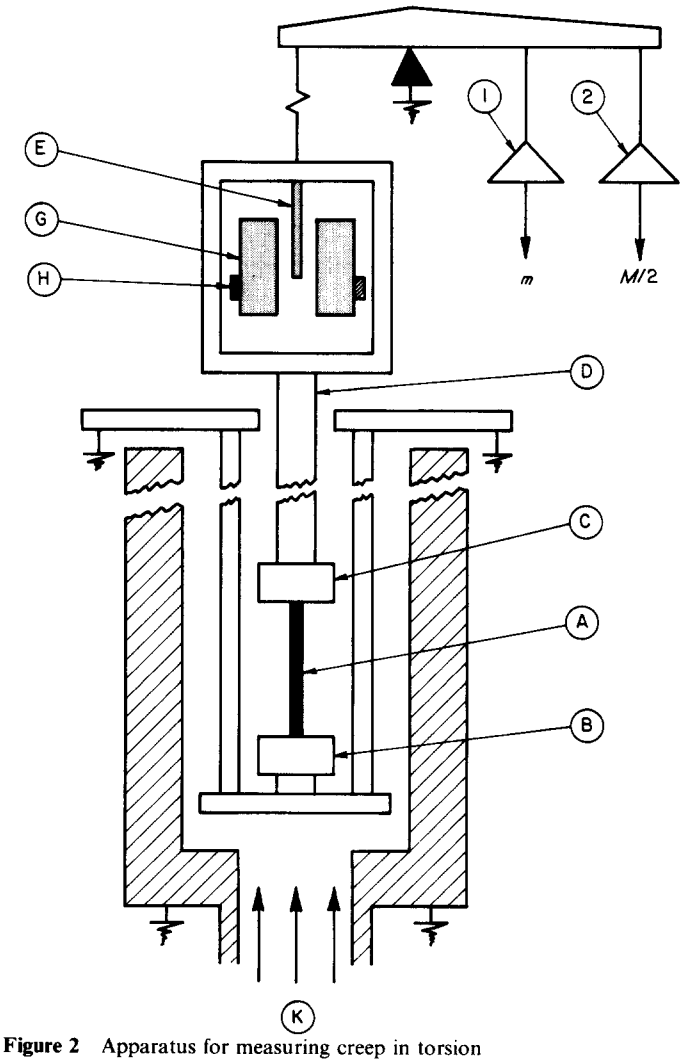

Figure 2 Apparatus for measuring creep in torsion

The voltage change developed per mm displacement was observed and the system thus simply and directly calibrated.

The principal experimental observation is $\Delta l(t)$ which was in the range 0 to 700 μm. After the specimen under the major force F had reached a state of pseudo-equilibrium the barrel was moved vertically—either by slipping it through the collar H, which was temporarily loosened for this purpose, or by turning the micrometer until the core was in the centre of the linear response range of the LVDT. The LVDT was then calibrated and the experiment initiated: the LVDT was used only in its linear range.

The specimen was surrounded by an insulated thermal jacket. Thermostated air, K, was blown vertically up over the specimen. The flow was generated by a fan which blew the air over a bank of controlled heating elements and then through a mixing system which comprised a plate containing a large number of small holes and finally a flow deflector to give the flow a swirl, as well as an upwards movement. The temperature was measured with six thermocouples placed in the gas and distributed evenly along the specimen.

The undeformed dimensions of the specimen were $l = 101$ mm $a = 9.76$ mm and $b = 2.10$ mm. It was glued into the clamps by means of Super-Glue: this system was recommended by the specimen manufacturers and performed perfectly. The temperature was never raised above 55°C. At the termination of each experiment the length of the specimen was determined by lowering the thermal jacket and measuring the length with a rule. The maximum value of l observed was 125 mm. For a specimen at this length it was important to measure the temperature with six thermocouples to obtain a significant average.

The specific experimental schedule was as follows. In the first experiment the specimen was loaded with $M = 634$ g and left overnight at T close to 50°C. The following morning a suitable state of pseudo-equilibrium had been achieved. The LVDT was adjusted into the centre of its linear range and a T-jump then performed 50.6°C→36.7°C, readings of Δl being obtained continuously on the chart recorder. The specimen was held at 36.7°C and the slow temperature induced secondary creep observed for 30 min. The specimen was then left at 36.7°C for several hours and a force-jump experiment then performed by placing a small mass of 9.025 g in pan 2 to yield $\Delta M = 18.05$ g: during this secondary creep experiment deflections were observed continuously for 30 min. This terminated experiment A. Subsequent experiments, labelled B to F, were then conducted in order with $M = 534$, 474, zero, 334 and 634 g. It was considered a more rigorous test of the theory to vary the load in this way, rather than to start at the highest load and work systematically downwards to zero, or *vice-versa*. For each experiment the specimen was loaded overnight to attain pseudo-equilibrium: the following day, as a rule, the T-jump experiment was performed in the morning and the F-jump in the afternoon. In each experiment the temperature jump was from close to 50°C to close to 37°C.

It is an assumption of the theory that when the specimen has been stretched to a state of pseudo-equilibrium under force $F = Mg$, that for small step-functions ΔM the specimen is linearly viscoelastic. This hypothesis was to be checked *inter alia* by the success or failure of the derived equations (equation (2.45)). It seemed nevertheless appropriate to examine the linearity directly using two well known techniques. In the first the specimen having been loaded with $M = 679$ g, for 100 h at 37°C was subjected to a series of step-functions (small ΔM) loading experiments each of 100 s duration with a period for recovery in between. Three experiments were performed at each ΔM: the loads used ranged from $\Delta M = 20.24$ g to $\Delta M = -10.19$ g. In the second test of linearity a test of the Boltzman superposition principle was made by predicting a four minute creep curve obtained for $\Delta M = 18.05$ g from an experiment in which this same mass is applied to the specimen in the following intermittent sequence. At $t = 0$, ΔM is applied and left on for 1 min: it is then removed for 1 min, re-applied for 1 min and removed for the final minute. From the values of $\Delta l(t)$ observed in this pulsed experiment the value of $\Delta l(t)$ observed in a constant ΔM experiment may be predicted. The agreement between a predicted and an observed 4 min $\Delta l(t)$ curve is an excellent test of the linearity of the specimen. In these experiments the length of the specimen was $l = 127$ mm and the values of $\Delta l(t)$ below 0.7 mm.

Torsion equipment

The torsional creep machine based on a design of McCrum and Morris[10], is shown in *Figure 3*. The specimen A is mounted between a fixed clamp B and a clamp C attached to a long torque tube, D. The torque tube is attached to a coil E, which lies in between the pole pieces (N and S) of a magnet and a core, F. A precise counterbalance G supports the assembly in a vertical position so that the tensile stress in the specimen is vanishingly small.

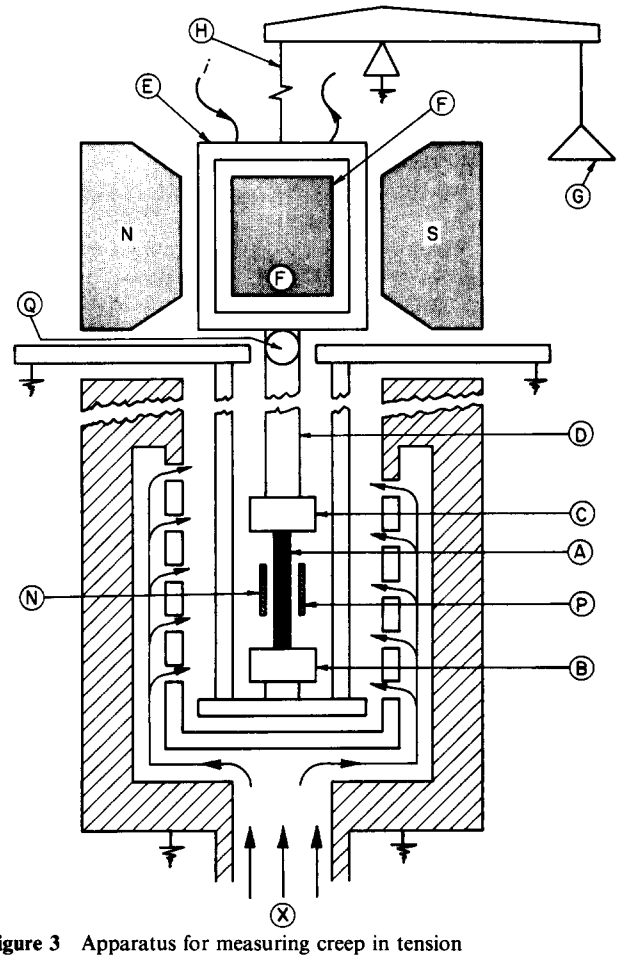

Figure 3 Apparatus for measuring creep in tension

When a current i is passed through the (of order 200) turns of the coil a torque Γ is generated. The torque is,

$$\Gamma = ki \tag{3.1}$$

in which k is the coil constant. The specimen and the support wire H are twisted: the torque in the support wire, which is of extremely small cross section, can be neglected in comparison to that in the specimen.

If a blade shaped specimen of length l, breadth a and thickness b is twisted by a constant torque Γ then, if the torque is applied at $t=0$,

$$\theta(t) = \frac{l\Gamma J(t)}{N} \tag{3.2}$$

$$N = \frac{1}{3}ab^3\left[1 - 0.63\left(\frac{b}{a}\right)\right] \tag{3.3}$$

This equation holds for a specimen which is linearly viscoelastic and for small values of θ: the problem of large values of θ and of non-linearity in the shear compliance, $J(t)$, is avoided by keeping $(\theta(t)/l)$ small. The specimen dimensions were $a=9.37$, $b=2.32$ and $l=52.9$ mm.

Suppose that a constant torque Γ is applied at T for a long period of time to reach a state of pseudo-equilibrium. A simultaneous jump in torque $\Gamma \rightarrow (\Gamma + \Delta\Gamma)$ and temperature $(T - \Delta T) \rightarrow T$ produces in a linear viscoelastic specimen a time dependent increment in rotation,

$$\Delta\theta(t) = \frac{l\Gamma}{N}\left[\frac{\Delta\Gamma}{\Gamma} - \beta^\circ \Delta T + \alpha \Delta T\right] J_R^T X^T(t)$$

The argument for this equation follows that used for equation (2.19): there is greater complexity since the stress varies across the cross-section of the blade, but the methods are identical. It follows then that if the two experiments are performed, as described in the theoretical section, one in which a measurement is made of $(\Delta\theta(t)/\Delta T)_\Gamma$ and in the other a measurement of $(\Delta\theta(t)/\Delta\Gamma)_T$, then (see equation (2.22)),

$$\left(\frac{\Delta\theta(t)}{\Delta T}\right)_i = i\left(\frac{\Delta\theta(t)}{\Delta i}\right)_T (\alpha - \beta^\circ) \tag{3.5}$$

since $\Gamma = ki$. This equation holds only for values of t sufficiently long that the perturbation due to an unsharp T-jump has been eliminated.

The rotation of the specimen is measured by reflecting a light beam from the concave mirror Q, *Figure 3*. If the throw of the optical lever is L, then a change in rotation $\Delta\theta$ is recorded as a deflection of the light spot Δx,

$$\Delta\theta = \frac{\Delta x}{2L}$$

The value of L used was 1820 mm so that,

$$\Delta\theta = 2.747 \times 10^{-4} \Delta x$$

The measurements of Δx were obtained using a Graphispot recorder. The position of the light spot was recorded continuously on chart paper throughout the course of the experiment.

The thermal-jacket for the torsion rig is shown in *Figure 3*. A thermostatted flow of pure nitrogen gas X, is generated by the method of Schwippert and van der Waal[11]. It flows into the specimen cavity through holes cut in the walls of the cavity, as shown. The temperature of the flowing gas is controlled by a large area platinum resistor (N) placed close to the specimen. The signal from the platinum resistor is monitored by a three term Eurotherm controller to bring the flowing gas to the correct temperature by means of a heater placed in the gas flow (not shown in *Figure 3*). The temperature of the specimen is obtained from another large area platinum resistor (P) placed in the gas close to the specimen. The Eurotherm controller is programmable in time and temperature and it was found that when a particular sequence of temperatures and times were set the temperatures were reproduced from experiment to experiment to within ± 0.1°C.

The experimental programme for the torsion experiments was as follows. The T-jump was scheduled to occur between 53°C and 39°C. To initiate the experimental programme the specimen was heated to 39°C (unstressed) and held at that temperature for a short time to record the zero for $\Gamma = 0$: a constant torque was then imposed by switching on a current of 0.80 mA. The torqued specimen was then heated to 72°C for 2 h and then cooled to 53°C for 2 h. The T-jump was then imposed, 53°C→39°C: the specimen was then held at 39°C for $1\frac{1}{2}$ h (values of $\Delta\theta$ being recorded continuously using the Graphispot). Values of $\Delta\theta(t)$ were obtained at 10, 15 and 20 min after the T-jump. The torque-jump experiment was then performed: whilst still at 39°C the current was dropped from 0.80 to 0.70 mA and the resulting creep recovery observed with the Graphispot. Values of $\Delta\theta(t)$ were obtained at 10, 15 and 20 min after the torque jump. The data points were then plotted according to equation (3.5). The specimen was then cooled to room temperature and left overnight with the torque current at 0.75 mA. The next day a temperature cycle, 1 h at 72°C, 2 h at 53°C with a T-jump to 35°C was followed with the current maintained at 0.75 mA: the torque-jump experiment was performed after 2 h at 39°C by dropping the current from 0.75 to 0.69 mA, the rotation being continuously recorded on the Graphispot. In this way a series of measurements at different values of i was obtained of $(\Delta\theta(t)/\Delta T)_i$ and of $i(\Delta\theta(t)/\Delta i)_T$ and plotted according to equation (3.5). The criterion in selecting times and temperatures was the essential time independence of θ before imposing the T-jump or the torque jump. The current was left on overnight, or over the weekend, at the value scheduled for the next experiment so as to facilitate the obtaining of the required state of pseudo-equilibrium.

RESULTS

Tensile experiments

Data for a typical experiment (Experiment B with $M = 534$ g) is shown in *Figure 4*, which shows the time dependence of:

(a) $(\Delta l(t)/\Delta T)_F$: this is the change in length at time t after the T-jump (51.4°C↓36.2°C) divided by ΔT (−15.2°C). The data recorded before 0.9 ks is not considered reliable, as will be illustrated below, because of the unsharp temperature step-function.

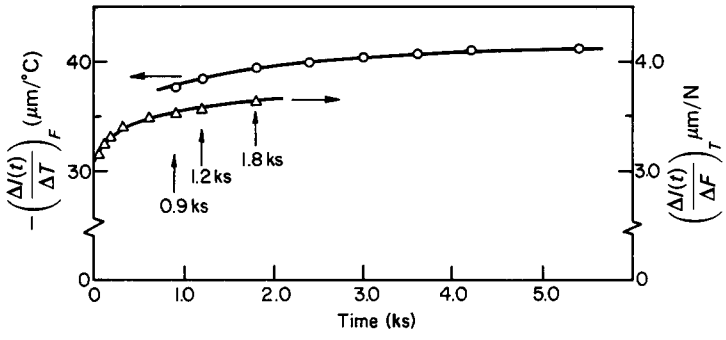

Figure 4 Results of T-jump and F-jump experiments for specimen under major load $M = 534$ g: $(\Delta l(t)/\Delta T)_F$ is the change in length at time t after the T-jump divided by $\Delta T = -15.2°C$ (51.4°C↓36.2°C): $(\Delta l(t)/\Delta F)_T$ is the change in length at $T = 36.2°C$ at time t after the F-jump divided by the value of ΔF. The order of experimentation was T-jump, then a ~10 ks delay for the zero to settle, followed by the F-jump

(b) $(\Delta l/\Delta F)_T$: this is the change in length at time t after the force-jump $(Mg\uparrow(M+\Delta M)g)$ divided by $\Delta F = g\Delta M = 9.81 \times 18.05$ N.

It will be seen in *Figure 4* that the creep generated by the T-jump continues significantly up to 6 ks after the T-jump. For this reason the force-jump experiment has to be delayed until of order 10 ks after the T-jump so that the zero is well defined. The deflections in the two experiments were of the same order of magnitude (at $t = 1.8$ ks, 600 μm and 642 μm in the T-jump and F-jump experiments respectively). For this particular value of the major mass ($M = 534$ g) linearity was checked in two subsidiary F-jump experiments using $\Delta M = 9.812$ g and then $\Delta M = 27.86$ g. The specimen was permitted to recover after each ΔM experiment with ΔM removed. For the three values of ΔM used, 9.812/18.05/27.86 g, the values of $\Delta l/\Delta M$ at 0.3 ks were (in μm/g),

$$\frac{324}{9.812}\Big/\frac{601}{18.05}\Big/\frac{926}{27.86} = 33.0/33.3/33.2 \qquad \text{(I)}$$

The overall length of the specimen under this value of $M = 534$ g and with the described thermal history (overnight $T \sim 50°C$) was $l = 122$ mm. The true strains were therefore, at 0.3 ks in the three ΔM experiments,

$$\frac{0.324}{122}\Big/\frac{0.601}{122}\Big/\frac{0.926}{122} = 0.0026/0.0049/0.0076 \qquad \text{(II)}$$

It is clear that the specimen is behaving in a linear manner (I) and that this is, perhaps, not surprising since the strains are well under 0.01 (II).

The time dependence of $(\Delta l/\Delta T)_F$ and $(\Delta l/\Delta F)_T$ is shown in *Figure 5* for the experiments A, B, C, E and F: experiment D was a thermal expansion experiment with $F = 0$. As the major load increases (from $M = 334$ g to $M = 634$ g) at a fixed time, both $(\Delta l/\Delta T)_F$ and $(\Delta l/\Delta F)_T$ increase: at fixed M both quantities show a slow increase (creep) with time.

In the governing equation (2.45) the major variable is F but nevertheless, data plotted at constant F and varying t should conform to equation (2.45). For experiment B values of $(\Delta l(t)/\Delta T)_F - l\beta_L^\circ$ are plotted in *Figure 6* against $F(\Delta l(t)/\Delta F)_T$ for values of t from 5 to 30 min. For values of t from 15 to 30 min the data conform well to the plotted (least-squares) straight line. This line is of slope,

$$(\alpha - \tfrac{2}{3}\beta^\circ) = -280.3 \pm 27.2 \times 10^{-5} °C^{-1}$$

we return later to consider this measure of α. It is clear that the rational prediction of equation (2.45) is obeyed for values of t in excess of 15 min. Below 15 min the data depart increasingly from the predicted linear relationship as t tends to lower and lower values. This departure is due to the lack of sharpness in the T-jump. This is supported by the data lying above the predicted line: because of the ramp in temperature $(T - \Delta T)\downarrow T$, $\Delta l(t)$ does not attain at values of t below 15 min the value it would have done if

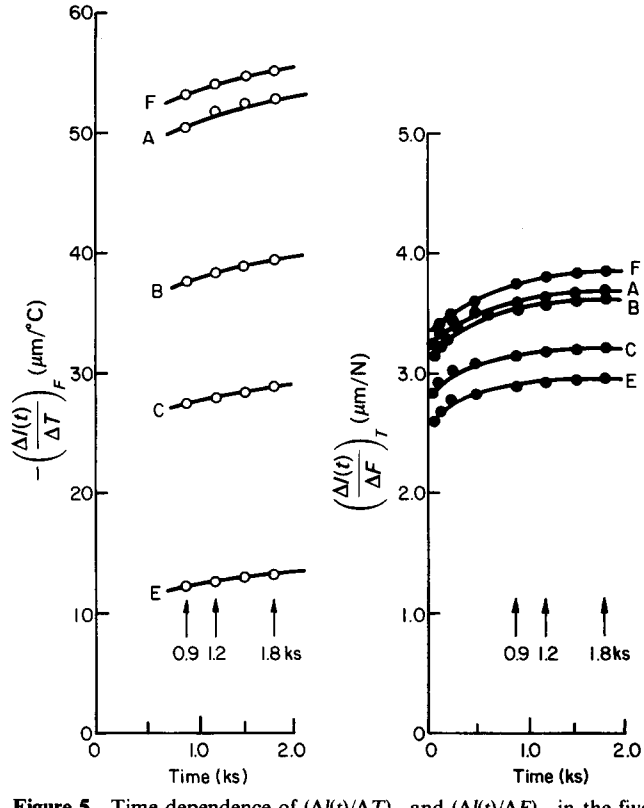

Figure 5 Time dependence of $(\Delta l(t)/\Delta T)_F$ and $(\Delta l(t)/\Delta F)_T$ in the five experiments. Values are taken from the data at 0.9, 1.2 and 1.8 ks for plotting according to equation (2.46). In the experiments the constant loads were 634 g (A), 534 g (B), 474 g (C), 334 g (E) and 634 g (F)

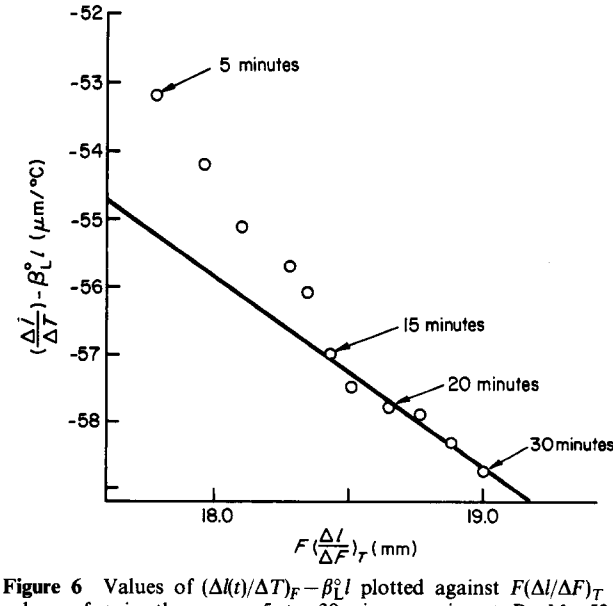

Figure 6 Values of $(\Delta l(t)/\Delta T)_F - \beta_L^\circ l$ plotted against $F(\Delta l/\Delta F)_T$ for values of t in the range 5 to 30 min: experiment B, $M = 534$ g, $\Delta M = 18.05$ g, $\Delta T = -15.2°C$. The systematic error due to the unsharp T-jump increasingly reduces as t moves from 5 to 15 min. At times above 15 min the data conform to the linear result predicted by equation (2.45). The line drawn is the least-squares fit to the data (15 min $< t <$ 30 min) and is of slope $(\alpha - 2\beta^\circ/3) = -280.3 \pm 27.2 \times 10^{-5}$ °C^{-1}

the step-function had been sharp. For t greater than 15 min the rate at which Δl increases with t becomes sufficiently low, that the systematic error due to the unsharp ramp becomes negligible.

A plot of $(\Delta l(t)/\Delta T)_F - l\beta_L^\circ$ against $F(\Delta l(t)/\Delta F)_T$ is given for experiments A, B, C, E and F in *Figure 7* for values of $t = 15$, 20 and 30 min: the single point $(\Delta l/\Delta T)_0$ from experiment D at $F = 0$ is also plotted. The line plotted through the points was obtained by least-squares and yields a slope which gives according to equation (2.45),

$$\alpha - \tfrac{2}{3}\beta^\circ = -313.2 + 2.5, \times 10^{-5}\text{°C}^{-1}$$

The value of $(\Delta l/\Delta T)_0$ leads to a determination of β_L°,

$$\beta_L^\circ = 15.8 \times 10^{-5}\text{°C}^{-1}$$

Assuming isotropy ($\beta^\circ = 3\beta_L^\circ$)

$$\beta^\circ = 47.4 \times 10^{-5}\text{°C}^{-1}$$

The value of α from this determination is therefore, for mean temperature $\bar{T} = 45°$,

$$\alpha = -281.6 \pm 2.5, \times 10^{-5}\text{°C}^{-1}$$

The quoted errors record the standard error of the slope in *Figure 7* and do not include other sources of error. We return to the discussion of errors later but it can be stated at once that the most likely cause of error is the determination of ΔT, the magnitude of the T-jump. It can be determined precisely at a point but the question is the averaging of the T-jump over the volume of the cavity occupied by the specimen.

The result of a linearity test at 37°C is shown in *Figure 8*. The major mass was $M = 679$ g and the length of the specimen was $l = 127$ mm. The required state of pseudo-equilibrium was achieved by maintaining the specimen at 37.7°C for 100 hours before the first ΔM experiments were initiated. *Figure 8* shows a plot of the generated changes in

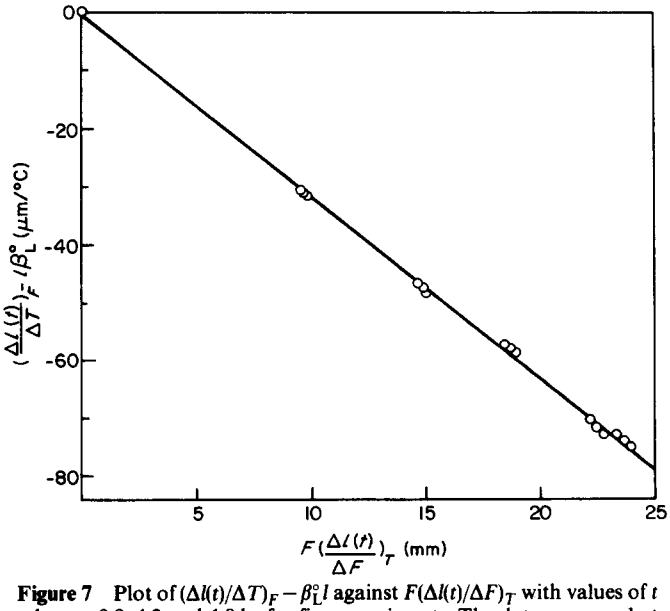

Figure 7 Plot of $(\Delta l(t)/\Delta T)_F - \beta_L^\circ l$ against $F(\Delta l(t)/\Delta F)_T$ with values of t taken at 0.9, 1.2 and 1.8 ks for five experiments. The data measured at $F = 0$ (thermal expansion data) is also plotted. The slope of the line, according to equation (2.45), is by least-squares $(\alpha - 2\beta^\circ/3) = -313.2 \pm 2.5, \times 10^{-5}\text{°C}^{-1}$. The linearity predicted by equation (2.45) at varying F and t is observed

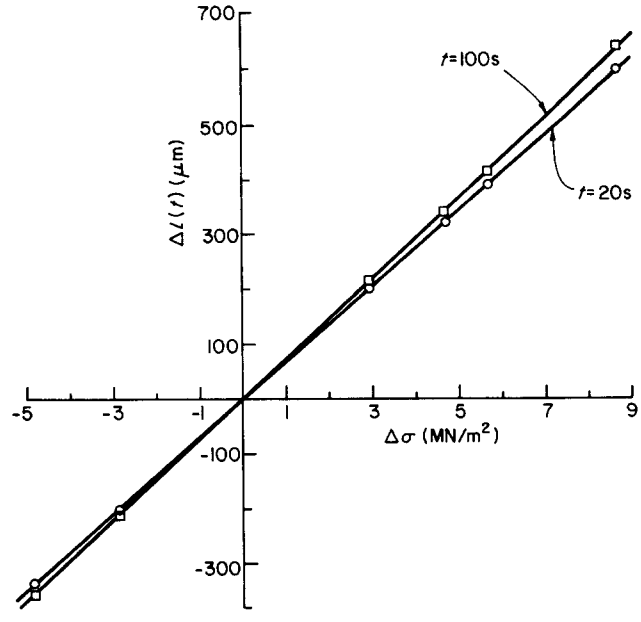

Figure 8 Linearity test showing an isochronal plot of elongations $\Delta l(t)$ for $t = 20$ and 100 s plotted against stress σ: temperature 37°C: specimen loaded for 100 h at 37°C by major mass $M = 679$ g before initiation of the experiments: the stress $\Delta\sigma = g\Delta M/A_0$, A_0 being the undistorted cross-section

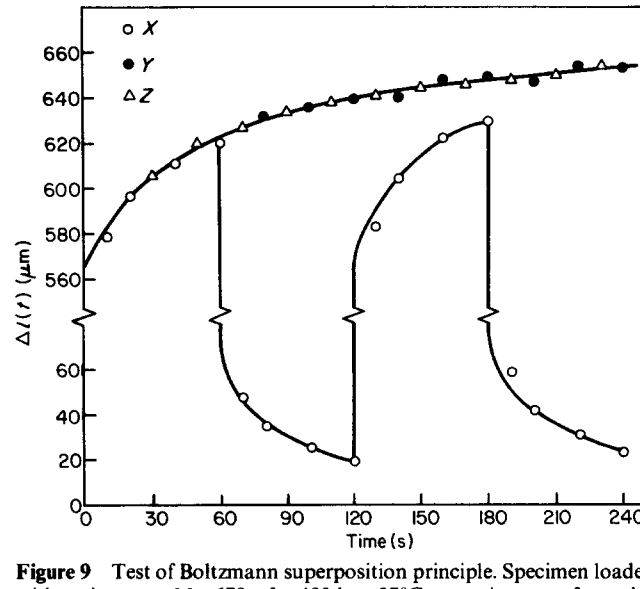

Figure 9 Test of Boltzmann superposition principle. Specimen loaded with major mass $M = 679$ g for 100 h at 37°C to attain state of pseudo-equilibrium. One minute pulses of $\Delta M = 18.05$ g (0–60 s and 120–180 s) produced values of $\Delta l(t)$, data X. Predicted values of $\Delta l(t)$ by Boltzmann superposition principle for a continuous application of $\Delta M = 18.05$ g, data Y. A determination of $\Delta l(t)$ for a continuous application of $\Delta M = 18.05$ g, data Z

length at $t = 20$ and 100 s after loading plotted against stress ($g\Delta M$ divided by the undistorted cross section of the specimen). It will be seen that the specimen exhibits excellent linear behaviour over the range of loads and extensions used. These loads and extensions were representative of the values in the experiments shown in *Figure 5*.

The results of the second test of linearity is shown in *Figure 9*. According to the Boltzmann superposition principle the relationship between the pulsed load and continuous load experiments is as follows. Consider the strains in the two experiments at times, x, $(x+60)$, $(x+120)$ and $(x+180)$ for $x < 60$ s. Let the strains in the pulsed experiment at these times be p, q, r and s. Let the strains in

the continuous load experiment at the same times be P, Q, R and S. According to the superposition principle,

$$P=p \qquad Q=p+q$$
$$R=q+r \qquad S=r+s \tag{4.1}$$

The values of $\Delta l(t)$ obtained in the pulsed experiment are given by data X, *Figure 9*. The prediction from data X according to equation (4.1) is given by data Y. The test of data Y is the experimental result of the continuous application of ΔM over 4 min, and this is given by data Z. The agreement between data Y and Z is excellent. We conclude that for small values of ΔM, such as that used (18.05 g with $M=679$ g) the elongations produced accord with the Boltzmann superposition principle.

Torsion

A plot of $(\Delta\theta/\Delta T)_\Gamma$ *versus* $\Gamma(\Delta\theta/\Delta\Gamma)_T$ is shown in *Figure 10*. The data shows points taken at $t=1.20$ ks after the T-jump or the torque-jump. The T-jump was 52.0°C↓37.4°C. As will be seen the data conform closely to the linear prediction of equation (2.22). From a least squares fit the slope yields,

$$\alpha-\beta^\circ=-309.3\pm4.1,\ \times 10^{-5}\text{°C}^{-1}$$

Using the value of β° determined in the tensile experiments yields,

$$\alpha=-261.9\pm4.1,\ \times 10^{-5}\text{°C}^{-1}$$

The limits reflect only the deviations on the slope taken from the least squares analysis. The T-jump was 52.0°C↓37.4°C which yields a mean temperature $\bar{T}=45$°C for this value of α.

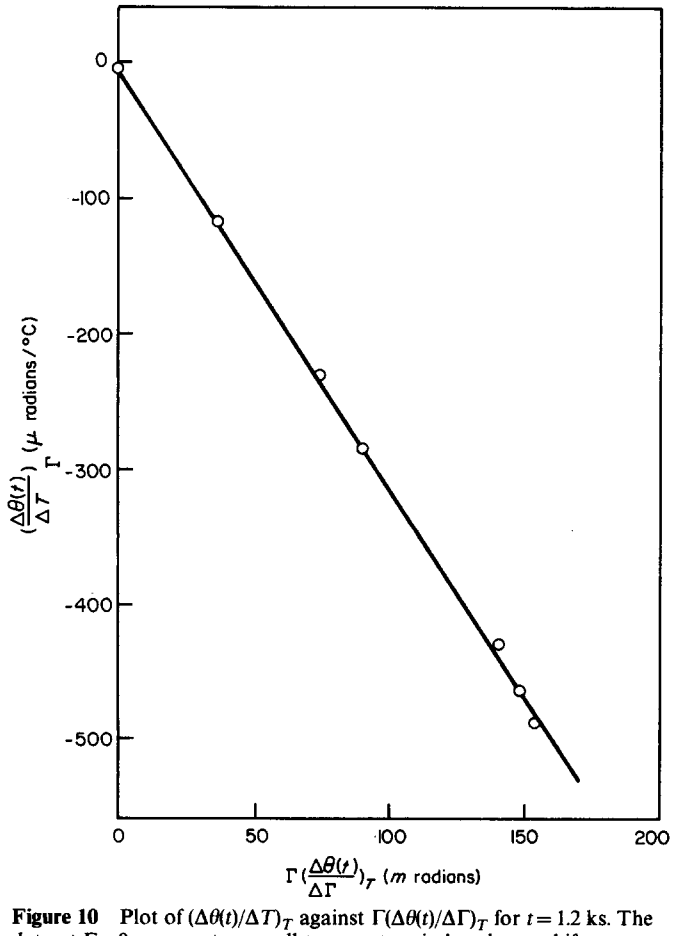

Figure 10 Plot of $(\Delta\theta(t)/\Delta T)_T$ against $\Gamma(\Delta\theta(t)/\Delta\Gamma)_T$ for $t=1.2$ ks. The data at $\Gamma=0$ represents a small temperature induced zero shift at zero torque. The slope of the line according to equation (2.22), is by least-squares $(\alpha-\beta^\circ)=-309.3\pm4.1$, $\times 10^{-5}$°C^{-1}. The linearity predicted by equation (2.22) for varying Γ is observed

DISCUSSION

The objective of our investigation has been the establishment of a rigorous theory of thermoviscoelastic deformation for an elastomer yielding a reliable measurement of α—and hence of κ and f_e/f—together with a test of the theory by experiment. The crucial reported tests are of:

(1) The relationship in tension between $(\Delta l(t)/\Delta T)_F-\beta_L^\circ l(t)$ and $F(\Delta l(t)/\Delta F)_T$, which should be linear for both arbitrary F and arbitrary t.

(2) The relationship in torsion between $(\Delta\theta(t)/\Delta T)_\Gamma$ and $\Gamma(\Delta\theta(t)/\Delta\Gamma)_T$, which should be linear for both arbitrary Γ and arbitrary t.

(3) The observed magnitude of α: the value should be independent of the observation method, tension or torsion, to within the error of the experiments.

Concerning (1) there is no doubt at all of the linearity for arbitrary F, as shown in *Figure 7*. The range of values of λ lay between 1.0 and 1.24. As shown in *Figure 6* when the perturbation due to the unsharp T-jump has diminished to the point of being negligible ($t>15$ min) the data at varying t and constant F fit reasonably well the slope predicted from the data with varying F: the slopes in *Figures 7* and *6* are respectively in units of 10^{-5}°C^{-1}, -313.2 ± 2.5 and -280.3 ± 27.2. The plot with t as variable at (constant F) does not give a reliable slope (note the standard error of ±27.2) since for the experimentally valid values of t (above 15 min) the rate at which $\Delta l(t)$ changes with t is so slow that experimental problems are considerable. These problems include minute shifts of the zero (due to previous thermal and mechanical history) and small temperature drifts (below 0.1°C) which—particularly at high F when the thermoelastic effect is large—can cause significant error. The most reliable figure for the slope comes, of course, from *Figure 7* (standard error ±2.5). The significance of the data with time as variable is that it is qualitatively consistent with the view that time has been taken into account correctly.

The stresses in the tensile experiments were kept to relatively low values to facilitate comparison with the torsion experiments. The tension experiments were conducted at primary stresses (F/A_0) in the range 0 to 300 kN/m^2. In torsion the primary shear stress varies from 0 at the centre of the cross section to a maximum, σ_{max}, at the centre of the wide edge: the greatest value of σ_{max} was 6 kN/m^2. The stresses generated in the step-function experiments were much closer in magnitude: in the tensile experiment in all cases this stress was $\Delta F/A_0=8.60$ kN/m^2: the maximum value of the step-function stress in the torsion experiments, was $\Delta\sigma_{max}\approx1$ kN/m^2. It is these latter stresses generated in the step-function experiments which determine whether or not the specimen response is linearly viscoelastic. It will be the subject of additional research in the future to determine if the equation of state, (equation (2.23)) holds at primary stresses above 300 kN/m^2 ($\lambda>1.24$).

The tensile and torsion values of α (in units of $10^{-5}°C^{-1}$, 281.6 ± 2.5 and 261.9 ± 4.1 respectively) differ by 7%, an amount which exceeds the quoted errors which come from the standard errors in the slopes (*Figure 7* and *10*). There are of course other errors. Of these most important is doubtless the systematic error in controlling and recording temperature. It is easy to control the temperature and to measure it at a point in a cavity: it is much more difficult to integrate these functions over the cavity volume. In the two experiments with different thermal systems and doubtless different temperature distributions within the cavities it is likely that the recorded values of ΔT were systematically in error from the true or integrated ΔT by amounts which would explain a good proportion of the 7% discrepancy in the values of α.

In the first experiment in torsion reported elsewhere[1], the value of t used in the step-function experiments was 10 min. It became clear during the present investigation that this time was too short. At 10 min after the T-jump the effect of the unsharp jump still perturbs the torsion data. The effect is exactly analogous to the effect in tension shown in *Figure 6*. It was found in torsion that at $t = 20$ min the perturbation due to the unsharp T-jump was erased and this was the time adopted. It is this change from $t = 10$ min to $t = 20$ min which accounts for the $\sim 15\%$ divergence in the values of α observed in the earlier torsion work and that reported here: in the earlier work measurements were not taken at $\bar{T} = 45°C$: extrapolation of the data at lower temperatures however, gives at $\bar{T} = 45°C$, $\alpha \sim -225 \times 10^{-5}°C^{-1}$. The torsion experiments are not well suited to experiments with t as a variable because the total T-jump induced rotation is very low at the small values of primary torque which may be applied in the equipment: if the primary torque is too high the torque inducing coil rotates out of the gap between magnet and core (*Figure 3*).

The large difference between the Shen formulation and that of this paper may be quickly illustrated. Shen's equation (equation (2.28)) is,

$$\beta_L^F = \beta_L^\circ + \left[\frac{\lambda^3 - 1}{\lambda^3 + 2}\right](\alpha - \beta_A^\circ) \tag{5.1}$$

Values of λ were computed at $t = 15$, 20 and 30 min by computing according to $\lambda = (l + \Delta l(t))/l_0$: β_L^F was computed according to $\beta_L^F = (1/l)(\Delta l(t)/\Delta T)$: l is the length of the specimen in the pseudo-equilibrium state observed to ± 0.5 mm. It will be seen in *Figure 11* that the plot of β_L^F against $(\lambda^3 - 1)/(\lambda^3 + 2)$ has serious defects. The first is that there is considerable scatter. This could be due to the observation of l. In our experiments the important determination was of $\Delta l(t)$ (following T-jump and F-jump) and this quantity was measured very accurately. The value of l was required with less accuracy and this was done as indicated in the Experimental section. The scatter could well be due to this cause but there are other possibilities. The Shen formulation does not account for time in any way. As t moves from 15 to 30 min β_L^F changes appreciably, as indicated in *Figure 11*: there is no change detectable in $(\lambda^3 - 1)/(\lambda^3 + 2)$ over this time interval.

It is otherwise when plotted according to the formulation of this paper. Dividing both sides of equation (2.45) by l yields,

$$\beta_L^F(t) = \beta_L^\circ + \left(\frac{F}{l}\right)\left(\frac{\Delta l(t)}{\Delta F}\right)_T(\alpha - \beta_A^\circ) \tag{5.2}$$

A plot of $\beta_L^F(t)$ against $(F/l)(\Delta l(t)/\Delta F)$ is shown also in *Figure 11*. Note that as $\beta_L^F(t)$ changes with t (each value of F has 3 recorded points, at $t = 15$, 20 and 25 min), $(F/l)(\Delta l(t)/\Delta F)_T$ changes also, so that $\beta_L^F(t)$ follows one line for arbitrary F and arbitrary t. The slope of the line in *Figure 11* according to the Shen equation yields

$$\alpha - \tfrac{2}{3}\beta^\circ = -244.6 \times 10^{-5}°C^{-1}$$

yielding

$$\alpha = -213.0 \times 10^{-5}°C^{-1}$$

This is a value quite different to those measured according to equation (2.45) (in tension) and to equation (2.22) (in torsion). It is clear that the Shen equation is invalid. It assumes that $f(\lambda)$ is given by equation (2.25), the Gaussian model, and this is not correct. We make no comments on the inadequacy of the Shen formulation in accounting for viscoelastic effects, which it is not designed to accomplish, and quite clearly does not.

The magnitude of κ is very sensitive to errors in α, since κ depends on the difference between two quantities, α and T^{-1}, of comparable magnitude, equation (1.4). For example for the tension value of $\alpha = -281.6 \times 10^{-5}°C$, obtained at temperature 45°C with $\beta^\circ/3 = 15.8 \times 10^{-5}$,

$$\kappa = [-281.6 + 314.3 - 15.8]\,10^{-5}°C^{-1}$$

$$= 16.9 \times 10^{-5}$$

The Shen value of α yields,

$$\kappa = [-213.0 + 314.3 - 15.8]\,10^{-5}°C^{-1}$$

$$= 85.5 \times 10^{-5}$$

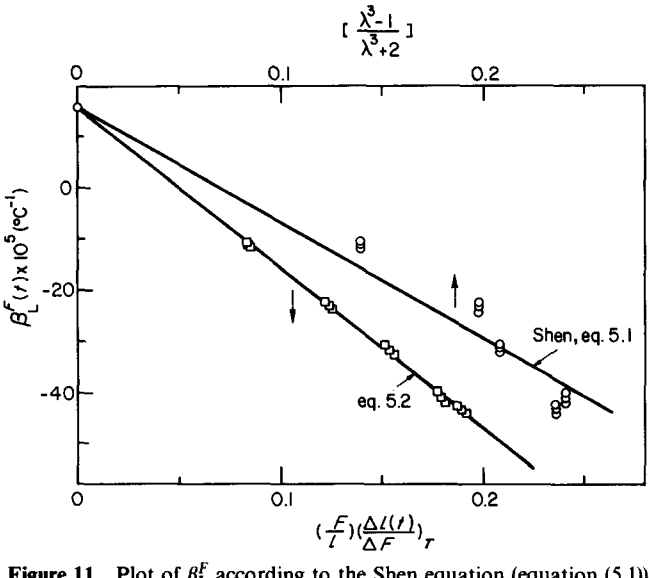

Figure 11 Plot of β_L^F according to the Shen equation (equation (5.1)) against $(\lambda^3 - 1)/(\lambda^3 + 2)$: slope $-225.8 \times 10^{-5}°C^{-1}$. Plot of $\beta_L^F(t)$ against $(F/l)(\Delta l/\Delta F)_T$ according to formulation of this paper (equation (5.2)): slope -313.2×10^{-5}. Six values of F (including $F = 0$): for each value of F data at three values of t, (15, 20 and 30 min). Note that the data follow equation (5.2) for arbitrary F and arbitrary t, a quality not shown when plotted according to the Shen equation

Of these two, for the reasons stated, the first is the most reliable.

There is no doubt that the thermoelastic experiment is, in principle, capable of deriving the highly significant macromolecular parameters α, κ and f_e/f and this fact has been known for many years. That small, often almost imperceptible, creep effects should imperil this highly desirable harvest doubtless lead to a certain exasperation, and the adoption of what can now be seen as inadequate methods. It could be said that the theory of rubber elasticity has been well-serviced and that it outran the slower development of thermoviscoelasticity. This was possibly inevitable since the intra-molecular phenomena, which are treated by the theory of rubber elasticity, are of simpler origin than the inter-molecular phenomena which control viscoelastic processes. The way ahead is pointed in this paper. It could be that others will find superior methods but the principle will remain: the deformation processes of elastomers, no matter how induced, are of thermoviscoelastic origin and this must be the basis of new experimental initiatives.

CONCLUSION

The methods of thermoviscoelasticity are shown to permit a precise determination of κ, the temperature dependence of the mean-square end-to-end length of a macromolecule. The basis of the experiment is the equivalence of the creep effects produced by T-jump and by force-jump. The force-jump experiment is used to calibrate the T-jump and so yield α the temperature coefficient of the relaxed shear compliance. The value of κ is then obtained from α using the theoretical result for the relaxed shear compliance. Conventional determinations of κ and of f_e/f are in error because the experiments are perturbed by viscoelastic effects.

REFERENCES

1 McCrum, N. G. *Polymer* 1984, **25** (*Commun.*), 213
2 Shen, M. *Macromolecules* 1969, **2**, 3538
3 Wolf, F. P. and Allen, G. *Polymer* 1975, **16**, 209
4 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, N.Y., Eighth Printing, 1971
5 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymer Solids', Wiley, New York, 1967
6 Mark, J. E. *Rubber Chem. Technol.* 1973, **46**, 593
7 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Third Edition, 1975, Clarendon Press, Oxford
8 McCrum, N. G. *Polymer* 1984, **25**, 309
9 Chai, C. K. and McCrum, N. G. *Polymer* 1984, **25**, 291
10 McCrum, N. G. and Morris, E. L. *Proc. Roy. Soc. A* 1964, **281**, 258
11 Schwippert, G. A. and Van der Waal, C. *Mikroniek*, July 1971