5978 *Macromolecules* **1995,** *28,* 5978−5980

Bulk Relaxations

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Received May 8, 1995

Introduction. In most applications of polymers where viscoelastic relaxations are of interest, the deviatoric viscoelasticity dominates, and the literature abounds with measurements and theory of shear relaxations. At times, however, the nondeviatoric, or bulk, stresses are critical. In highly constrained geometries such as adhesive joints, bulk stresses are generated during nonisothermal operation if a mismatch in adhesive and substrate coefficients of thermal expansion exists. Appreciable volume changes can occur during prolonged annealing at temperatures slightly below the nominal glass transition temperature which can significantly change the stress level.

Therefore, there is a real need for a constitutive equation for compressible, viscoelastic polymers in which the bulk relaxations are properly described. This paper presents a new approach to one aspect of the bulk relaxations, stress relaxation in response to a step temperature change.

Linear Elasticity. Constitutive equations may be formulated in terms of stress or strain. The stress formalism defines moduli and is more convenient for analyzing stress relaxation experiments. The strain formalism defines compliances and is more convenient for analyzing creep experiments. The stress formalism will be adopted in the following discussions since the tensor can be input directly into the momentum balance in commercial finite element codes.

The stress tensor, $\boldsymbol{\sigma}$, can be decomposed into a deviatoric component $\mathbf{D}$ and a diagonal component $-P\mathbf{I}$, where P is the thermodynamic pressure, such that $\boldsymbol{\sigma} = \mathbf{D} - P\mathbf{I}$. In a purely elastic, isotropic material for which the total strain is small,

$$\mathbf{D} = 2G\left[\gamma - \left(\frac{1}{3}\mathrm{tr}\gamma\right)\mathbf{I}\right] \tag{1}$$

$$-(P - P_0) = K[\mathrm{tr}\gamma - \Delta_{V_{\mathrm{th}}}] = K\mathrm{tr}\gamma_{\mathrm{eff}} \tag{2}$$

where γ is the infinitesimal strain tensor, G is the shear modulus, K is the bulk modulus, $\mathrm{tr}\gamma$ is the total volumetric strain, $\Delta_{V_{\mathrm{th}}} = \alpha(T - T_0)$ is the volumetric strain due to simple thermal expansion (where α is the coefficient of thermal expansion), and P_0 is the pressure at the reference temperature, T_0, and in the unstrained state. The strain, $\Delta_{V_{\mathrm{th}}}$, must be subtracted off from any imposed strain since the reference state of strain is the material at T_0.

Examine only the pressure for now. Equation 2 originates from tracking the increment in pressure arising from imposed strain and temperature increments.

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}T \tag{3}$$

Since

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \tag{4}$$

and the bulk modulus and coefficient of thermal expansion are defined by

$$K = -V\left(\frac{\partial P}{\partial V}\right)_T \quad \text{and} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{5}$$

Equation 3 can be rewritten as

$$-\mathrm{d}P = K\frac{\mathrm{d}V}{V} - K\alpha\,\mathrm{d}T \tag{6}$$

from which eq 2 is recovered upon integration.

Linear Viscoelasticity. To describe linear viscoelastic behavior, one usually adopts the Boltzmann superposition principle.[1] The deviatoric stress then is represented by

$$\mathbf{D} = 2\int_{-\infty}^{t}\mathrm{d}s\; G(t-s)\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\gamma - \left(\frac{1}{3}\mathrm{tr}\gamma\right)\mathbf{I}\right)\right] \tag{7}$$

in which the shear relaxation modulus is defined. For thermorheologically simple polymers in nonisothermal operation, one must properly account for the change in mobility with temperature, and eq 7 becomes

$$\mathbf{D} = 2\int_{-\infty}^{t}\mathrm{d}s\; G\left(\int_{s}^{t}\frac{\mathrm{d}u}{\Omega(u)}\right)\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\gamma - \left(\frac{1}{3}\mathrm{tr}\gamma\right)\mathbf{I}\right)\right] \tag{8}$$

where $\Omega(u)$ is the ratio of the monomeric friction at the system temperature at time u to the friction at some reference temperature at which the function $G(t)$ is experimentally determined. Numerous experiments have validated this basic approach.

The pressure in a viscoelastic system can be determined straightforwardly for isothermal operation

$$-(P - P_0) = \int_{-\infty}^{t}\mathrm{d}s\; K(t-s)\left[\frac{\mathrm{d}}{\mathrm{d}t}(\mathrm{tr}\gamma)\right] \tag{9}$$

in which the bulk relaxation modulus is defined. Again, numerous experiments have validated this isothermal formalism, albeit most have examined volume changes upon pressure jumps.

Nonisothermal operation is more complex, however, due to the $(\partial P/\partial T)_V$ term in eq 3. If we write $P = P_V + P_T$ where P_V represents the $(\partial P/\partial V)_T$ contribution and P_T represents the $(\partial P/\partial T)_V$ contribution, we reason that

$$-(P_V - P_{V_0}) = \int_{-\infty}^{t}\mathrm{d}s\; K\left(\int_{s}^{t}\frac{\mathrm{d}u}{\Omega(u)}\right)\left[\frac{\mathrm{d}}{\mathrm{d}t}(\mathrm{tr}\gamma)\right] \tag{10}$$

in analogy with eq 8. P_T is elusive.

Historical Treatment of Bulk Nonisothermal Viscoelasticity. The community has historically attacked P_T by referring to equation 6. Using $\mathrm{d}(\Delta_{V_{\mathrm{th}}}) = \alpha\,\mathrm{d}T$ as the natural strain, we can proceed as before

$$-(P - P_0) = \int_{-\infty}^{t}\mathrm{d}s\; K\left(\int_{s}^{t}\frac{\mathrm{d}u}{\Omega(u)}\right)\left[\frac{\mathrm{d}}{\mathrm{d}t}(\mathrm{tr}\gamma - \Delta_{V_{\mathrm{th}}}(s))\right] \tag{11}$$

Unfortunately, to be consistent in this formulation of the problem, the time dependence of the thermal strain arises not only from the time dependence of the external temperature profile but from the creep retardation spectrum as well.

[†] Supported by the United States Department of Energy under Contract No. DE-AC04-94AL85000.

0024-9297/95/2228-5978$09.00/0

A typical approach[2] assumes that the thermal strain can be approximated by

$$\Delta_{V_{\mathrm{th}}}(t) = \int_{T_{\mathrm{f}}(t)}^{T(t)} \mathrm{d}T' \, \alpha_{\mathrm{g}}(T') + \int_{T(0)}^{T_{\mathrm{f}}(t)} \mathrm{d}T' \, \alpha_{\mathrm{r}}(T') \quad (12)$$

where α_g and α_r are the glassy and rubbery coefficients of thermal expansion and T_f is the fictive temperature in which the effects of the creep retardation spectrum are hidden. T_f has, then, its own evolution equation.

Proposed Treatment of Bulk Nonisothermal Viscoelasticity. Let us step back a minute and examine exactly what we are trying to determine. We can separate the pressure problem into two, well-defined experiments. In the first experiment, we instantaneously, isothermally, and hydrostatically squeeze a polymer and watch the time dependence of the pressure [i.e., determine $(\partial P/\partial V)_T$]. In the second experiment, we take the same polymer, instantaneously raise its temperature by a couple degrees *while holding the volume constant*, and watch the time dependence of the pressure [i.e., determine $(\partial P/\partial T)_V$]. It is in this second experiment that the differences between the historical and proposed approaches will become apparent.

The two approaches agree in their predictions for the results of the first experiment. Since the instantaneous volumetric strain displaces the mean position of the atoms, we expect a slow rearrangement of polymer configurations to accommodate the new conditions. Indeed, the bulk modulus has been shown to decay from a "glassy" bulk modulus to a "rubbery" bulk modulus in a roughly power law ($t^{-1/4}$) form.[1]

In the second experiment, the historical formalism (eq 11) predicts a similar slow approach to equilibrium in response to the temperature jump. However, let us step back from the formalism and examine this experiment anew. No mean displacement of atoms has occurred; we have simply made them "wiggle" faster. Consequently, no time dependence of the pressure is obvious. In fact, over the temperature range proposed for this experiment, one wonders if any configurational rearrangement would occur. Therefore, a reasonable guess for the results of the second experiment would propose that the pressure responds immediately to the instantaneous temperature jump with no further time dependence. We now have distinctly different predictions for a given experiment from the two approaches.

From these discussions, we hypothesize that the pressure can be calculated by

$$P - P_0 = \Psi[T(t) - T_0] - \int_{-\infty}^{t} \mathrm{d}s \, \mathrm{K}\left(\int_{s}^{t} \frac{\mathrm{d}u}{\Omega(u)}\right)\left[\frac{\mathrm{d}}{\mathrm{d}t}(\mathrm{tr}\gamma)\right] \quad (13)$$

where Ψ is $(\partial P/\partial T)_V$. If Ψ were truly constant, the value of Ψ could be obtained by evaluating the product $K\alpha$ at room temperature. Comparing eqs 11 and 13, we can appreciate the great simplification of the proposed formulation. Equation 11 involves nested integrals with a dummy variable, T_f, encumbered with its own evolution equation, whereas eq 13 replaces this complexity with an easily evaluated constant.

Is this formulation reasonable? As an extreme test, we can examine $\Psi = K\alpha$ as it passes through the glass transition. Since K decreases while α increases through the transition by approximately compensating magnitudes (a lack of accurate experimental data hinders more exact analysis), the formulation appears to pass this test. Since temperature and time are complementary, the initial and final magnitudes of $\Psi = K(t)\,\alpha(t)$ are also approximately equal. While this reasoning does not prove that the intermediate time response is constant, it does suggest that, if Ψ is time dependent, its variation is small. Therefore, since the historical approach requires considerable experimental data with attendant imprecision while the proposed approach requires only a constant, any minor error in the proposed approach is countered by its ease of implementation.

Remember also that we are focusing on the time dependence of Ψ. While we have argued that, in addition to its time independence, Ψ is only a weak function of temperature, one may easily include a stronger temperature dependence.

Nonlinearities. While somewhat outside the point of this paper, nonlinearities must be mentioned. Since the polymer community views relaxation rates as dependent on "free volume", it is clear that changes in volume, as in a volumetric creep experiment, will affect the free volume and the relaxation rates. Therefore, the bulk relaxation rates must be temperature and volume dependent arising from their intrinsic free volume dependence. With this addition, the well-known asymmetry in volumetric creep when quenched to a given temperature from above and below[3] is qualitatively understood. The usual form assumed for the relaxation times contains, in general, three terms

$$\tau = A + \frac{E_\tau}{RT} + \frac{CV}{V - V_0} \quad (14)$$

The first term is related to the limiting relaxation time at infinite temperature. The second term is simply an Arrhenius relationship. The third term is the Vogel–Fulcher, WLF, or free volume relationship expressed without specific reference to temperature (V_0 is the "occupied volume", usually assumed to be a constant).

Straying even farther from this paper's purpose, the shear modulus relaxation rates will also depend on "free volume". Now, the phenomenon of "physical aging" can be addressed.[3] The formalism of deviatoric nonlinearities is extremely complex and, as yet, not fully resolved.

Experimental Predictions of the Proposed Approach. The proposed and historical formalisms agree in their predictions of isothermal experiments. Therefore, predictions of volumetric creep in response to a pressure jump are unchanged. Similarly, predictions of pressure relaxation in response to a volume jump are unchanged.

As we examined above, the predictions of the two formalisms differ for the pressure during a temperature jump at constant volume. The historical approach predicts a slow equilibration, and the calculation is not trivial and requires considerable material characterization. The proposed formalism predicts an instantaneous (certainly much faster than any bulk modulus relaxation) pressure response. Unfortunately, these particular experiments have not been performed due to their inherent complexity.

Can the proposed formalism correctly predict volumetric creep in response to a temperature jump? For an instantaneous temperature jump of $T_1 - T_0$ at $t = 0$, eq 13 reduces to

$$\Psi[T_1 - T_0] = \int_0^t \mathrm{d}s \, K(t-s) \frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{tr}\gamma(s)] \quad (15)$$

which is identical to the response to an imposed isothermal hydrostatic pressure, P,

$$P - P_0 = -\int_0^t \mathrm{d}s\, K(t-s)\, \frac{\mathrm{d}}{\mathrm{d}t}\, [\mathrm{tr}\gamma(s)] \qquad (16)$$

Both eqs 15 and 16 can be solved implicitly for the volumetric creep, and the corresponding "compliances", in response to either an applied pressure or temperature jump, are identical in the linear viscoelastic regime. This equivalence between the time dependence of the volumetric creep in response to pressure or temperature jumps is expected and observed experimentally.[1]

As an aside, this observation suggests an alternate path for deriving the proposed formalism of eq 13. Instead of assuming no time dependence to the $(\partial P/\partial T)_V$ term, we could have equivalently assumed that the linear compliances just mentioned (from temperature or pressure jump experiments) have identical time dependences. This hypothesis, as shown in eqs 15 and 16, yields constant Ψ and, therefore, eq 13.

Returning to the predictions of the proposed approach, eq 13 reproduces the asymmetry in volumetric creep when quenched from above and below to a given temperature if the appropriate free volume dependence is incorporated into the bulk and shear relaxation times. For example, immediately after an instantaneous temperature jump, the volume is $V(0+) = V_0[1 + \alpha_g \Delta T]$. Since the final volumes in the two temperature jump experiments are identical, the volumes during the course of the two experiments are always different. Since the retardation rates depend sensitively on the volume (i.e., free volume), the observed asymmetry in volumetric creep is recovered.

Conclusions. The proposed formalism for bulk relaxations differs from the historical approach in its treatment of viscoelastic effects in the term $(\partial P/\partial T)_V$. The proposed approach argues that this term has a negligible time dependence, whereas the historical approach invokes a complicated set of nested integral equations to determine its time evolution. Both formalisms require that the bulk and shear relaxation rates depend on free volume.

Acknowledgment. I thank Bob Chambers of Sandia National Laboratories for his stimulation and guidance on this topic.

References and Notes

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MA950613+