

The Coupling of Deformations in a Class of Viscoelastic Solids to Temperature Changes

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Synopsis

A class of viscoelastic materials is defined by the parametric constitutive equations $\sigma = \sigma(\epsilon, t)$ and $T = T(\epsilon, t)$. It is shown that the creep rates and relaxation rates of such materials are determined by their thermal properties and the ambient temperature, and that the assumptions of constant stress or strain respectively and constant temperature are incompatible.

The straining of solids in the elastic range is not accompanied by any sensible development of heat, but plastic and other deformations involving hysteresis or any other forms of nonreversibility are always accompanied by considerable rises of temperature. High polymers which neck down to smaller cross sections in the manner described as "cold drawing" can reach high temperatures at the shoulders of the "neck," temperature differences of 80°C having been estimated for amorphous poly(ethylene terephthalate).¹ Similar effects in crystalline polymers such as gutta-percha, nylon, and polyethylene are well known. The heating of metals during plastic deformation is equally well known in other fields of study.

Because nonelastic deformations involve loss of mechanical energy, these must always result in the development of heat. If the heat is allowed to raise the temperature of the material being strained, a greater or smaller change will be apparent in its mechanical properties, depending upon the temperature sensitivity of these properties in the material in question. Thus, at a temperature in the vicinity of the glass transition point, very considerable changes may be expected if isothermal conditions are not maintained. Marshall and Thompson¹ have shown, for example, that poly(ethylene terephthalate), extended adiabatically from 20°C, behaves rather as though it were extended isothermally at 80°C once an extension ratio of 4 was reached. Jones and Beeson² showed that rubber, stretched isothermally, is stronger than when it is stretched adiabatically, and that the difference can be ascribed to a temperature rise of up to 10°C which was observed by other workers between these two modes of stretching.

It is, therefore, of general interest to study the coupling between the two processes of deformation and heating. This has previously been studied by a number of authors including Zener,³ Biot,⁴ and Gruntfest,⁵ but it is felt that the following considerations throw additional light on the subject.

At this stage, the constitutive equations of the anelastic materials being deformed are not defined except insofar as they represent a state of quasi-equilibrium, $\sigma = \sigma(\epsilon, T, t)$. It is assumed that for such materials, the stresses developed in any mode of straining may be parameterized and written as $\sigma = \sigma(\epsilon, t)$, while at the same time the temperature attained is also a function of the strain and elapsed time; thus, $T = T(\epsilon, t)$, which depends also on ambient conditions. Graphs of $\sigma = \sigma(\epsilon, t)$, such as that given by Turner,⁶ are known in the literature, but these are not considered by him in conjunction with any imposed or resultant constant temperature field.

In order that $\sigma = \sigma(\epsilon, t)$ may be single valued, (compare Bridgeman⁸), a limitation is here imposed such that the stress is attained by first applying the strain or the increment of strain, always in the same way, e.g., by means of a step function or ramp function, followed by a period of relaxation however short. The stress and temperature functions *taken simultaneously* are proposed as constitutive assumptions for a class of viscoelastic materials with straining and relaxation in the sequence stated. What follows is, therefore, applied only to materials behaving in this way.

In a simple tensile experiment, the total differentials of stress and temperature may then be written as

$$d\sigma = \left(\frac{\partial\sigma}{\partial\epsilon}\right)_t d\epsilon + \left(\frac{\partial\sigma}{\partial t}\right)_\epsilon dt \quad (1)$$

and

$$dT = \left(\frac{\partial T}{\partial\epsilon}\right)_t d\epsilon + \left(\frac{\partial T}{\partial t}\right)_\epsilon dt. \quad (2)$$

Now, by definition, $(\partial\sigma/\partial\epsilon)_t$ is the isochronous modulus, or Young's modulus E , in the tensile mode. In other modes of deformation, the relevant moduli will be used. At $t = 0$, E_0 will be an "instantaneous" or "zero" modulus, and at $t = \infty$, it will be the equilibrium modulus. We write

$$(\partial\sigma/\partial\epsilon)_t = E \quad (3)$$

and define

$$(\partial\sigma/\partial t)_\epsilon = -r = \text{relaxation rate} \quad (4)$$

and

$$(\partial T/\partial t)_\epsilon = -\theta = \text{cooling rate.} \quad (5)$$

θ is a function of the thermal insulation applied and the diffusivity of the material, and of the geometry of the specimen, since an internal material point cannot cool down at the same rate as a point on the surface.

At constant stress, $d\sigma = 0$, and eq. (1) leads to

$$d\sigma = -r dt + E d\epsilon = 0 \quad (1a)$$

or

$$(\partial\epsilon/\partial t)_\sigma = r/E \quad (6)$$

and by substitution into eq. (2) we obtain

$$(\partial T/\partial\epsilon)_\sigma = (\partial T/\partial\epsilon)_t + (\partial T/\partial t)_\epsilon (\partial t/\partial\epsilon)_\sigma. \quad (7)$$

Since $(d\epsilon/\partial T)_\sigma = \alpha$, the coefficient of linear expansion, we have

$$1/\alpha = (\partial T/\partial \epsilon)_t - E\theta/r \tag{8}$$

from which

$$\left(\frac{\partial T}{\partial \epsilon}\right)_t = \frac{1}{\alpha} + \frac{E\theta}{r}. \tag{9}$$

Similarly, we obtain

$$\left(\frac{\partial \epsilon}{\partial t}\right)_r = -\frac{(\partial T/\partial t)_\epsilon}{(\partial T/\partial \epsilon)_t} = \frac{\alpha r \theta}{E\theta\alpha + r} = \frac{r}{E + r/\alpha\theta} \tag{10}$$

and

$$\left(\frac{\partial \sigma}{\partial t}\right)_r = -\frac{r^2}{E\theta\alpha + r} = -\frac{r}{1 + E\alpha\theta/r}. \tag{11}$$

If these are compared with eqs. (6) and (4), respectively, it will be seen that the creep rate at constant temperature is smaller than that at constant stress. Similarly, the relaxation rate at constant temperature is smaller than it is at constant strain. Note that if $r = 0$, that is, the material has no relaxation under given strain, it will not creep under a given load.

These statements may not appear reasonable at first sight. However, it should be understood that, if as a result of a relaxation process at constant strain a change of temperature takes place, this will affect the stress directly by counteracting the tendency to expand or contract.

If, in a second experiment, these changes are allowed to proceed in thermal isolation from the surroundings, we have

$$dQ = \sigma d\epsilon - \rho dT = 0 \tag{12}$$

where ρ is the heat capacity per unit volume. Operating as before between eqs. (12) and (1) and (2), we obtain the following expressions:

$$\left(\frac{\partial T}{\partial t}\right)_Q = -\bar{\theta} = +\frac{\sigma r}{E\rho} \tag{13}$$

the signs indicating that in an adiabatic experiment, the temperature rises as would be expected:

$$\left(\frac{\partial \epsilon}{\partial t}\right)_Q = \frac{r\sigma\alpha}{E\rho} = \frac{\bar{\theta}r\rho\alpha}{E\bar{\theta}\rho\alpha - \sigma r\alpha + \rho r} \tag{14}$$

$$\left(\frac{d\sigma}{dt}\right)_Q = r\left(\frac{\sigma\alpha}{\rho} - 1\right) = \frac{-r^2(\rho - \sigma\alpha)}{E\bar{\theta}\rho\alpha - \sigma r\alpha + \rho r} \tag{15}$$

from which we have

$$E_Q = \left(\frac{\partial \sigma}{\partial \epsilon}\right)_Q = \frac{r\left(\frac{\sigma}{\rho} - \frac{1}{\alpha}\right)}{\bar{\theta}} = E\left(1 - \frac{\rho}{\sigma\alpha}\right). \tag{16}$$

The adiabatic creep and relaxation in eqs. (14) and (15) are essentially different from those for the isothermal condition given in (6) and (4), in that the former depend explicitly upon the stress.

It is instructive and illuminating to compare the creep rates and relaxation rates for a simple material such as a Maxwell solid. In describing the behavior of such a solid, Maxwell⁷ specified a material which relaxes at a rate proportional to the stress, but he made no mention of the thermal conditions under which the relaxation takes place. We assume that relaxation takes place at constant strain and that the rate of cooling is proportional to the temperature difference between the actual temperature of the sample (T) and the ambient (T_0), i.e., $\theta = b(T - T_0)$. The coefficient b , therefore, measures the efficiency of heat removal in a very thin sample, or the diffusivity in a thick sample, or a combination of both. We, therefore, have (the superscript M indicating a Maxwell body)

$$\left(\frac{\partial\sigma}{\partial t}\right)_\epsilon^M = -\frac{\sigma}{\tau} \quad (17a)$$

$$\left(\frac{\partial\sigma}{\partial t}\right)_T^M = -\frac{\sigma}{\tau} \cdot \frac{1}{1 + E\alpha b\tau/\sigma} = -\frac{\sigma}{\tau} \cdot \frac{\sigma}{\sigma + E\alpha b(T - T_0)\tau} \quad (17b)$$

$$\left(\frac{\partial\sigma}{\partial t}\right)_\rho^M = -\frac{\sigma}{\tau} \cdot \frac{1}{1 + E\alpha b\tau\rho/\sigma(\rho - \sigma\alpha)} = -\frac{\sigma}{\tau} \cdot \frac{\sigma}{\sigma + \frac{E\alpha b\rho(T - T_0)}{\rho - \sigma\alpha}} \quad (17c)$$

In the order given, these three expressions with $T > T_0$ and $\sigma < \rho/\alpha$ form a series of decreasing relaxation rates. It is instructive to note that when either an isothermal test or an adiabatic test is commenced with the sample maintained at ambient temperature throughout, the relaxation rates observed will be identical with that obtained at constant extension. However, this is a physical impossibility since a finite sample cannot cool on its surface at the same rate as at an internal point, and therefore a Maxwell body and, by extension, any viscoelastic body cannot relax at constant strain and constant temperature at the same time. If $\sigma > \rho/\alpha$, the adiabatic relaxation rate becomes larger than the isothermal or constant-strain relaxation rate.

Also, for creep,

$$\left(\frac{\partial\epsilon}{\partial t}\right)_\sigma^M = \frac{\sigma}{E\tau} \quad (18a)$$

$$\left(\frac{\partial\epsilon}{\partial t}\right)_T^M = \frac{\sigma}{E\tau} \cdot \frac{1}{1 + \sigma/E\alpha b\tau} \quad (18b)$$

$$\left(\frac{\partial\epsilon}{\partial t}\right)_\rho^M = \frac{\sigma}{E\tau} \cdot \frac{1}{1 + \sigma(\rho - \sigma\alpha)/E\alpha b\tau} \quad (18c)$$

It is important to note that under isothermal or adiabatic conditions, neither the relaxation rate nor the creep rate is proportional to the stress. It follows that the superposition principle cannot be invoked under these conditions.

As an example of the effects to be expected, the following figures have been calculated, using data from published tables for a commercial co(polyacetal),⁹ we have, at a tensile stress of 100 kg/cm²,

$$\rho = 0.25 \text{ cal}/^\circ\text{C}\cdot\text{cc}$$

$$\alpha = 10^{-4}/^\circ\text{C}$$

$$E = 21000 \text{ kg/cm}^2$$

and assuming that the material behaves as a Maxwell body,

$\left(\frac{\partial\sigma}{\partial t}\right)_\epsilon$	$\text{for } \theta = 10^\circ\text{C/hr}$	$\text{for } \theta = 20^\circ\text{C/hr}$
	$-241.5 \text{ kg/cm}^2 \cdot \text{hr}$	$-241.5 \text{ kg/cm}^2 \cdot \text{hr}$
$\left(\frac{\partial\sigma}{\partial t}\right)_r$	$-205 \text{ kg/cm}^2 \cdot \text{hr}$	$-222 \text{ kg/cm}^2 \cdot \text{hr}$
$\left(\frac{\partial\sigma}{\partial t}\right)_q$	$-191 \text{ kg/cm}^2 \cdot \text{hr}$	$-206 \text{ kg/cm}^2 \cdot \text{hr}$

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