

# Stresses and volume changes in a polymer loaded axially in a rigid die

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We consider the boundary value problem of an isotropic, linearly elastic or linearly viscoelastic material constrained in a rigid die and loaded by a uniform axial stress  $\sigma_{33}$  ('piston/die' problem). The elastic solution is obtained in terms of the shear and bulk modulus of the material, and the Laplace-transformed form of the viscoelastic solution in terms of the Laplace transforms of the shear and bulk relaxation moduli. Solutions to the viscoelastic problem at  $t=0$  and for  $t \rightarrow \infty$  are found, which involve only values of the relaxation moduli at these times. The complete solutions in time space for a viscoelastic material which has a time-independent bulk modulus, and behaves like a Maxwell or Voigt model in shear, are calculated and discussed. For typical elastic and solid viscoelastic materials, the volume change in the 'piston/die' situation is only 60–80% of that observed in the hydrostatic case with  $P = -\sigma_{33}$ . The 'piston/die' geometry is therefore not a universally applicable method for pressure–volume–temperature (PVT) studies. Methods in which a material is subjected to true hydrostatic pressures (achieved through the use of a confining fluid) must be preferred.

(Keywords: rigid die; axial stress; viscoelasticity; bulk modulus)

## INTRODUCTION

Within the theories of linear elasticity<sup>1</sup> and linear viscoelasticity<sup>2,3</sup>, the responses of a material to shear stresses and to a hydrostatic pressure provide the most fundamental mechanical characterization possible. We wish to analyse and compare the solutions of the mechanical boundary value problems that underlie two techniques commonly used to study the response of the volume of a polymer to pressure<sup>4,5</sup>, also known as pressure–volume–temperature (PVT) studies.

In one of the techniques<sup>6–9</sup> the material is subjected to a true hydrostatic pressure through the use of a confining fluid, often mercury. In the other technique<sup>10–13</sup>, a sample is placed in a die or cylinder, and a force is applied to one end of the sample with a piston. In this type of experiment, it is always implied, or explicitly stated, that the sample is subjected to a pressure  $P = F/A$ , in which  $F$  is the force applied to the piston, and  $A$  the cross-sectional area. As long as the sample is a true liquid, this is certainly a correct statement. However, it is not correct when the sample has any kind of solid-like character, such as polymers in the glassy, semicrystalline and melt state. One of us (PZ) has pointed this out previously<sup>4,5</sup>. This paper will analyse this situation in some detail, and will compare volume changes measured in a 'piston/die' type of experiment with those obtained under true hydrostatic conditions.

We will first discuss a solution to the 'piston/die' problem for a linear elastic material. Using the correspondence principle between elasticity and viscoelasticity<sup>3</sup>, the solution to the elastic problem will then be transformed into a solution of the linear viscoelastic problem. Linear viscoelasticity has been shown to be a good description of polymers in a variety of states<sup>2</sup> (glassy, semicrystalline and melt), and some very

general conclusions regarding the behaviour of a polymeric material constrained in a die can be drawn from our analysis without reference to specific materials. For two specific material models (Maxwell and Voigt elements) complete solutions will be derived and discussed.

## STATEMENT OF PROBLEMS

### 'Piston/die' problem

An isotropic material is placed into a die or cylinder with zero clearance and no friction between sample and die wall. The axis of the die is parallel to the  $x_3$  direction. The die is assumed to be rigid. A force  $F(t)$  is applied to the free end of the sample in the  $x_3$  direction, and is evenly distributed over the area  $A$ . We will allow this force to be a function of time. This has no particular consequences for an elastic material: all stresses and strains will depend only on the instantaneous value of the force. However, for a viscoelastic material the stresses and strains at a given time are determined by the entire past history of these quantities.

### Hydrostatic problem

The material is subjected to a hydrostatic pressure  $P(t)$ . This is achieved in practice by surrounding it with a liquid under pressure<sup>6–9</sup>.

### Materials description

We will describe a linear elastic material<sup>1</sup> by its shear and bulk moduli, and the linearly viscoelastic material<sup>2,3</sup> by its shear relaxation modulus  $G(t)$  and its bulk relaxation modulus  $K(t)$ . We will further assume that all material constants ( $G$  and  $K$ ) or material time functions [ $G(t)$  and  $K(t)$ ] are independent of the state of stress; in particular, they are assumed to be independent of the hydrostatic component of the stress state. The latter is not

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a good assumption for polymers. Young's<sup>14,15</sup> and bulk moduli<sup>4,5,14,16</sup> clearly depend strongly on pressure—in fact, one of the reasons for doing PVT work is to investigate the pressure dependence of the bulk modulus, or its inverse, the compressibility. We are ignoring these complications, for which there is no place in the linear theories of elasticity and viscoelasticity.

### SOLUTION OF THE LINEAR ELASTIC PROBLEM

From the symmetry of the 'piston/die' problem, it is clear that the  $x_3$ -axis and any two axes perpendicular to it form a principal axis system. We immediately find  $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_T = 0$  (rigid die), and  $\sigma_{33}(t) = F(t)/A$ .

Substituting  $\sigma_{33}(t)$  and the known strain components into the fundamental equations of elasticity<sup>1</sup> relating stress and strain, yields the only unknown strain component:

$$\varepsilon_{33}(t) = \frac{3}{3K + 4G} \sigma_{33}(t) \quad (1)$$

Since  $\varepsilon_{33}$  is the only non-vanishing strain component, it is equal to the relative volume change:

$$\frac{\Delta V}{V}(t) = \varepsilon_{33}(t) = \frac{3}{3K + 4G} \sigma_{33}(t) \quad (2)$$

The transverse stresses  $\sigma_T(t) = \sigma_{11}(t) = \sigma_{22}(t)$  can next be obtained

$$\sigma_T(t) = \frac{3K - 2G}{3K + 4G} \sigma_{33}(t) \quad (3)$$

For the linearly elastic material, it is thus clear that the state of stress is not hydrostatic, since the transverse principal stresses  $\sigma_T$  are not equal to the third principal stress  $\sigma_{33}$ .

The elastic solution to the hydrostatic problem is given directly by the definition of the bulk modulus:

$$\frac{\Delta V}{V} = -\frac{P}{K} \quad (4)$$

It is instructive to compare the ratio  $R_v$  of the volume change in the material in the die under the axial stress  $\sigma_{33}(t) = F(t)/A$  (equation (2)) to that experienced when the same material is subjected to a hydrostatic pressure  $P(t) = -\sigma_{33}(t)$ , see equation (4):

$$R_v = \frac{\Delta V(\text{die})}{\Delta V(\text{hydrostatic})} = \frac{3}{3 + 4G/K} \quad (5)$$

The results are given in Table 1 for a range of values of the ratio  $G/K$ . Also listed in Table 1 are the values of the Poisson ratio  $\nu$  that correspond to the ratios of the moduli, as well as the ratio of transverse to axial stresses,  $R_s$ :

$$R_s = \frac{\sigma_T}{\sigma_{33}} = \frac{3 - 2G/K}{3 + 4G/K} \quad (6)$$

From Table 1 it is concluded that for a material with a reasonable value of the Poisson ratio (0.25 to 0.4 for most

structural metals) the volume changes in the 'piston/die' experiment are 20–40% smaller than those under a hydrostatic stress with  $P = -\sigma_{33}$ . In all fairness, the 'piston/die' method has not been applied extensively to metals or other elastic materials, except by surrounding the sample with a sleeve of a soft (plastically deformable) material, such as indium or lead.

We will next proceed to find a solution for a viscoelastic material and discuss if the use of the 'piston/die' method can be better justified for a viscoelastic material, such as a polymer.

### SOLUTION OF THE VISCOELASTIC PROBLEM

From a solution of an elastic boundary value problem, the solution to the corresponding viscoelastic problem may be found through the application of the so-called correspondence principle<sup>3</sup>. Applied to our situation, the Laplace-transformed viscoelastic solution is found by (1) replacing  $G$  and  $K$  in the elastic solution with  $s\bar{G}(s)$  and  $s\bar{K}(s)$ , respectively (where the bar over the function denotes the Laplace transform<sup>17</sup> and  $s$  is the Laplace variable), and (2) replacing the stresses and strains (or applied forces or displacements) with their Laplace transforms. The final solution can then be obtained (at least in principle) by inverting the Laplace-transformed solution.

Applied to our 'piston/die' problem, we obtain from equations (1)–(3) the following:

$$\bar{\varepsilon}_{33}(s) = \frac{3}{3s\bar{K}(s) + 4s\bar{G}(s)} \bar{\sigma}_{33}(s) \quad (7)$$

$$\frac{\Delta \bar{V}}{\bar{V}}(s) = \bar{\varepsilon}_{33}(s) \quad (8)$$

$$\bar{\sigma}_T(s) = \frac{3s\bar{K}(s) - 2s\bar{G}(s)}{3s\bar{K}(s) + 4s\bar{G}(s)} \bar{\sigma}_{33}(s) \quad (9)$$

To obtain a full solution by inversion requires a knowledge of the time dependence of the applied force  $F(t)$ , yielding  $\bar{\sigma}_{33}(s)$ , and the material functions  $K(t)$  and  $G(t)$ , yielding  $\bar{K}(s)$  and  $\bar{G}(s)$ , respectively. We will now do this for the simple cases of the Maxwell and Voigt models.

**Table 1** Elastic material constrained in a rigid die: Poisson ratio  $\nu$ , ratio  $R_s = \sigma_T/\sigma_{33}$  of transverse stress  $\sigma_T$  to axial stress  $\sigma_{33}$ , and ratio  $R_v$  of the volume change to the volume change under hydrostatic conditions (with  $P = -\sigma_{33}$ ), as a function of ratio of shear modulus  $G$  to bulk modulus  $K$ . The same table may be used for a viscoelastic material at  $t=0$  and for  $t \rightarrow \infty$ , provided  $G/K$  is re-interpreted as the ratio of the shear and bulk relaxation moduli at these times,  $G(0)/K(0)$  and  $G_\infty/K_\infty$ , respectively (see text)

$G/K$	$\nu$	$R_s$	$R_v$
0.00	0.500	1.000	1.000
0.01	0.495	0.980	0.987
0.05	0.475	0.906	0.938
0.10	0.452	0.824	0.882
0.20	0.406	0.684	0.789
0.30	0.364	0.571	0.714
0.40	0.324	0.478	0.652
0.50	0.286	0.400	0.600
0.60	0.250	0.333	0.556
0.70	0.216	0.276	0.517

General solution of the viscoelastic problem at  $t=0$  and for  $t \rightarrow \infty$

It is possible to obtain a solution at  $t=0$ , and for  $t \rightarrow \infty$  involving only the shear and bulk relaxation moduli at these times. This requires the use of the initial value and the final value theorems of Laplace transforms<sup>17</sup>. The initial value theorem states:

$$Q(0) = \lim_{s \rightarrow \infty} s\bar{Q}(s) \quad (10)$$

and the final value theorem:

$$\lim_{t \rightarrow \infty} Q(t) = \lim_{s \rightarrow 0} s\bar{Q}(s) \quad (11)$$

When applying the two limiting value theorems, it is useful to introduce the distinction between viscoelastic liquids and viscoelastic solids. A viscoelastic material is called a viscoelastic liquid in shear, if its shear relaxation modulus decays to zero as  $t \rightarrow \infty$ :

$$G(t) \rightarrow 0 \text{ for } t \rightarrow \infty \quad (12)$$

A similar expression involving the bulk relaxation modulus could be used to define a viscoelastic liquid in bulk deformation, but no such material is expected to exist.

A viscoelastic solid in shear and bulk deformation, respectively, is characterized by relaxation moduli which do not decay to zero at  $t \rightarrow \infty$ . In that case it is convenient to write the relaxation moduli as a sum of a time-dependent part and the asymptotic value for  $t \rightarrow \infty$ :

$$G(t) = G_\infty + G^+(t) \quad \text{with } G^+(t) \rightarrow 0 \text{ for } t \rightarrow \infty \quad (13a)$$

$$K(t) = K_\infty + K^+(t) \quad \text{with } K^+(t) \rightarrow 0 \text{ for } t \rightarrow 0 \quad (13b)$$

Applying the initial value theorem to equations (7) and (8) yields:

$$\frac{\Delta V}{V}(0) = \lim_{s \rightarrow \infty} s \frac{\overline{\Delta V}}{V}(s) = \lim_{s \rightarrow \infty} \left[ \frac{3s\bar{\sigma}_{33}(s)}{3s\bar{K}(s) + 4s\bar{G}(s)} \right]$$

$$\frac{\Delta V}{V}(0) = \frac{3\sigma_{33}(0)}{3K(0) + 4G(0)} \quad (14)$$

Similarly, applying the initial value theorem to equation (9) yields:

$$\sigma_r(0) = \frac{3K(0) - 2G(0)}{3K(0) + 4G(0)} \sigma_{33}(0) \quad (15)$$

Both results (14) and (15) are reminiscent of the elastic results (2) and (3), except that equations (14) and (15) apply at  $t=0$  only and the elastic constants  $K$  and  $G$  are replaced by the zero-time values of the relaxation functions  $G(t)$  and  $K(t)$ .

The viscoelastic analogue of equation (4) (using the correspondence principle) is:

$$-\bar{P}(s) = s\bar{K}(s) \frac{\overline{\Delta V}}{V}(s) \quad (16)$$

Applying the initial value theorem to this equation yields:

$$-P(0) = \lim_{s \rightarrow \infty} s\bar{P}(s) = \lim_{s \rightarrow \infty} s\bar{K}(s) s \frac{\overline{\Delta V}}{V}(s)$$

$$\frac{\Delta V}{V}(0) = -\frac{P(0)}{K(0)} \quad (17)$$

This is again reminiscent of the corresponding elastic result (equation (4)).

As a consequence of the analogy between the elastic result and the viscoelastic result at  $t=0$ , Table 1 can be used unchanged for the viscoelastic material at  $t=0$ , making only the re-interpretation that the first column on the left now represents the ratio of the  $t=0$  values of the shear relaxation modulus and the bulk relaxation modulus,  $G(0)/K(0)$ .

The short-time values of viscoelastic relaxation functions of polymers are commonly determined by standardized mechanical tests, such as tensile tests, torsion tests, etc., lasting a few minutes. Results of such tests are not normally reported as viscoelastic functions, but simply as 'elastic constants', similar to those of elastic materials.

When one looks over the available data for short-time shear and bulk moduli, it is apparent that the ratio  $G(0)/K(0)$  is 0.5 to 0.2 for solid polymers. From Table 1, this leads to a short-time volume change for the 'piston/die' experiment 20–40% below that of the hydrostatic experiment. The differences are very similar to those expected for typical metal samples. On the other hand, a soft rubbery material, or a polymer melt, might have a bulk modulus as much as 20 times larger than its  $t=0$  shear modulus. This would imply systematic errors in the  $t=0$  volume change of just a very few per cent, which is likely comparable with experimental error inherent in either the PVT method or a 'piston/die' experiment. For this type of material, the 'piston/die' method can yield acceptable results.

This discussion of the  $t=0$  volume change can be complemented by a similar discussion of the  $t \rightarrow \infty$  behaviour. Application of the final value theorem to equation (8), (9) and (13) yields:

$$\lim_{t \rightarrow \infty} \frac{\Delta V}{V} = \frac{3 \lim_{t \rightarrow \infty} \sigma_{33}(t)}{3 \lim_{t \rightarrow \infty} K(t) + 4 \lim_{t \rightarrow \infty} G(t)} = \left( \frac{3}{3K_\infty + 4G_\infty} \right) \lim_{t \rightarrow \infty} \sigma_{33}(t) \quad (18)$$

$$\lim_{t \rightarrow \infty} \sigma_r(t) = \left( \frac{3K_\infty - 2G_\infty}{3K_\infty + 4G_\infty} \right) \lim_{t \rightarrow \infty} \sigma_{33}(t) \quad (19)$$

These equations are once again identical in form to the elastic results (2) and (3), except that the bulk modulus  $K$  and shear modulus  $G$  have been replaced by the  $t \rightarrow \infty$  limits of the bulk and shear relaxation functions, respectively. Again, Table 1 can be used, this time with the re-interpretation of the  $G/K$  ratio at  $G_\infty/K_\infty$ . What we said above about the applicability of the 'piston/die' method at  $t=0$  could be repeated here for  $t \rightarrow \infty$ .

At intermediate times (and for a constant applied force) the volume change and transverse stresses will increase monotonically from the  $t=0$  value to the higher  $t \rightarrow \infty$  values. The volume change ratio  $R_v$  will reach unity for any material that is a viscoelastic liquid in shear, since, in

(Note that the Voigt model is a viscoelastic solid, with  $G_\infty = G^0$ .)

The Laplace transform of the shear relaxation modulus of the Voigt model becomes:

$$\bar{G}(s) = \frac{G^0}{s} + G^0 t_1 \quad (23)$$

These expressions are returned to equations (7)–(9), also observing that  $\bar{K} = K/s$  and  $\bar{\sigma}_{33} = \sigma_{33}^0/s$ , since  $K$  and  $\sigma_{33} = \sigma_{33}^0$  are constants. The following equations are obtained:

*Maxwell model*

$$\bar{\varepsilon}_{33}(s) = \frac{\Delta V}{V} = \frac{3\sigma_{33}^0}{s[3K + 4G^0s(s + 1/t_1)^{-1}]} \quad (24)$$

$$\bar{\sigma}_T(s) = \frac{3K - 2G^0s(s + 1/t_1)^{-1}}{s[3K + 4G^0s(s + 1/t_1)^{-1}]} \sigma_{33}^0 \quad (25)$$

*Voigt model*

$$\bar{\varepsilon}_{33}(s) = \frac{\Delta V}{V} = \frac{3}{s(3K + 4G^0 + 4G^0 t_1 s)} \sigma_{33}^0 \quad (26)$$

$$\bar{\sigma}_T(s) = \frac{3K - 2G^0 - 2G^0 t_1 s}{s(3K + 4G^0 + 4G^0 t_1 s)} \sigma_{33}^0 \quad (27)$$

These Laplace-transformed relations are easily inverted by standard methods<sup>17</sup>, with the final results given by:

*Maxwell model*

$$\frac{\Delta V}{V}(t) = \frac{\sigma_{33}^0}{K} \left[ 1 - \frac{4G^0}{3K + 4G^0} \exp\left(-\frac{3K}{3K + 4G^0} \left(\frac{t}{t_1}\right)\right) \right] \quad (28)$$

$$\sigma_T(t) = \sigma_{33}^0 \left[ 1 - \frac{6G^0}{3K + 4G^0} \exp\left(-\frac{3K}{3K + 4G^0} \left(\frac{t}{t_1}\right)\right) \right] \quad (29)$$

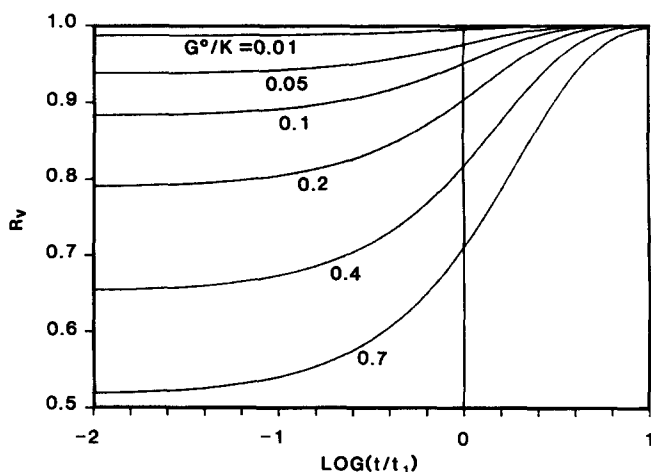
*Voigt model*

$$\frac{\Delta V}{V}(t) = \frac{3\sigma_{33}^0}{3K + 4G^0} \left[ 1 - \exp\left(-\frac{3K + 4G^0}{4G^0} \left(\frac{t}{t_1}\right)\right) \right] \quad (30)$$

$$\sigma_T(t) = \frac{\sigma_{33}^0}{3K + 4G^0} \left[ 3K - 2G^0 - \frac{9}{2} K \exp\left(-\frac{3K + 4G^0}{4G^0} \left(\frac{t}{t_1}\right)\right) \right] \quad (31)$$

First, we wish to point out that these solutions have the required values at  $t=0$  and for  $t \rightarrow \infty$ . This is easily confirmed by inspection, and is also apparent from Figures 1 and 2. These figures show the time dependence of the volume change ratio  $R_v$ , defined as before as the ratio of the relative volume change in the piston/die experiment to the relative volume change under hydrostatic conditions with  $P = -\sigma_{33}^0$ , given by equation (4) for a time-independent bulk relaxation modulus.

As expected of any viscoelastic liquid in shear, the Maxwell model reaches  $R_v = 1$  for  $t \rightarrow \infty$ , but starts out with much lower values at  $t=0$ , which depend on the



**Figure 1** Ratio  $R_v$  of the volume change in the piston/die problem (constant applied stress  $\sigma_{33}^0$ ) to that experienced under hydrostatic stress (with  $P = -\sigma_{33}^0$ ) as a function of the ratio of time  $t$  to relaxation time  $t_1$ , for a material with a time-independent bulk modulus and the shear relaxation modulus of a Maxwell model. Parameter  $G^0/K$ : ratio of the spring constant of the Maxwell model to the bulk modulus

that case  $G_\infty = 0$ . Thus, for a viscoelastic liquid, the volume change in the 'piston/die' experiment will eventually reach the value obtained under hydrostatic conditions. Similarly, the transverse stresses will increase with time, reaching  $\sigma_{33}$  ( $R_s = 1$ ) after an infinitely long time for a viscoelastic liquid.

Although the results for  $t=0$  and  $t \rightarrow \infty$  were shown to be identical to the elastic results, with the appropriate moduli at those times substituted for the constants  $K$  and  $G$ , this does not hold for arbitrary times. If results for intermediate times are desired, the relations in equations (7)–(9) must be inverted to obtain the full solutions. This requires a knowledge of the materials function  $G(t)$  and  $K(t)$  for all times.

*Complete solutions for Voigt and Maxwell models*

We will derive complete solutions for two simple cases. We will assume a constant axial stress  $\sigma_{33} = F_0/A = \sigma_{33}^0$  applied in the 'piston/die' problem. We will also assume a material that has a time-independent bulk relaxation modulus  $K$  (which is an excellent approximation<sup>2</sup>), and behaves either like a Maxwell or Voigt element<sup>2,3</sup> in shear. A Maxwell element consists of a spring (spring constant  $G^0$ ) and a dashpot (damper with viscosity  $\eta$ ) in series. In the Voigt element these two basic components are connected in parallel.

The shear relaxation modulus for the Maxwell model is:

$$G(t) = G^0 \exp(-t/t_1) \quad \text{with} \quad t_1 = \eta/G^0 \quad (20)$$

(Note that the Maxwell model is a viscoelastic liquid.)

The Laplace transform of the shear relaxation modulus of the Maxwell model becomes<sup>17</sup>:

$$\bar{G}(s) = G^0 \frac{1}{s + 1/t_1} \quad (21)$$

The shear relaxation modulus of the Voigt element is:

$$G(t) = G^0 + G^0 t_1 \delta(t) \quad \text{with} \quad t_1 = \eta/G^0 \quad (22)$$

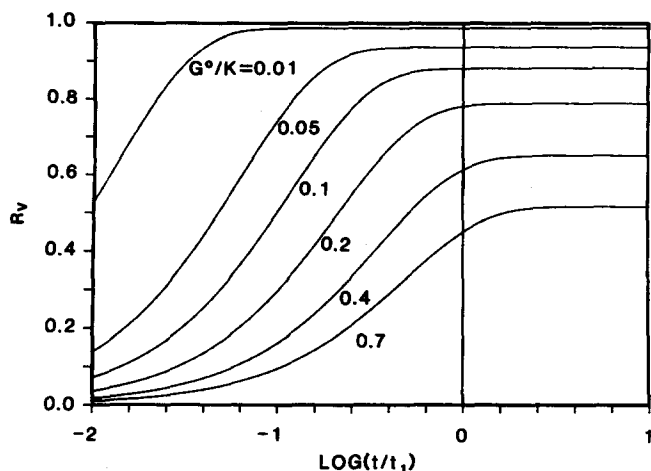


Figure 2 Ratio  $R_v$  of the volume change in the piston/die problem (constant applied stress  $\sigma_{33}^0$ ) to that experienced under hydrostatic stress (with  $P = -\sigma_{33}^0$ ) as a function of the ratio of time  $t$  to retardation time  $t_1$ , for a material with a time-independent bulk modulus and the shear relaxation modulus of a Voigt model. Parameter  $G^0/K$ : ratio of the spring constant of the Voigt model to the bulk modulus

ratio of the shear spring constant  $G^0$  to the bulk modulus  $K$ .

The Voigt model, on the other hand starts out with  $R_v = 0$ . This is a consequence of the infinitely high shear relaxation modulus at  $t = 0$ . For  $t \rightarrow \infty$ ,  $R_v$  reaches constant values, as expected for a viscoelastic solid, with asymptotic values identical to those derived from our discussion of equation (18), with  $G_\infty = G^0$ . At intermediate times, the volume change ratio increases for both models.

For both the Maxwell and the Voigt models it is instructive to look at the values of  $R_v$  at  $t = t_1$ , i.e. after one relaxation (or retardation) time. These differ substantially from unity, except for  $G^0 \ll K$ . Thus, even for a material that is a viscoelastic liquid, and eventually reaches  $R_v = 1$ , the 'hydrostatic limit' is only approached after several relaxation times. In 'piston/die' experiments one may thus expect a time dependence of the volume change (i.e. the piston position), which lasts for a very long time, even though the bulk behaviour is elastic, i.e. has no time dependence. By contrast, compression experiments using a confining fluid show no time dependence at all under the same assumption (although real materials may show a time dependence, since their bulk deformation may not be totally elastic<sup>2</sup>).

## CONCLUSIONS

The 'piston/die' method<sup>10-13</sup> does not generally represent a good method for determining the response of materials to pressure. For elastic materials the method yields acceptably low systematic errors for the volume change (less than 6%) only if the ratio of shear to bulk modulus is smaller than about 0.05, i.e. for materials with a Poisson ratio above about 0.475. For viscoelastic materials (such as polymers) the error is above 6% at  $t = 0$

and for  $t \rightarrow \infty$ , unless the ratio of the shear to the bulk relaxation modulus at the respective times is less than 0.05. This effectively limits the use of this technique to very soft rubbers and polymer melts, but excludes its use for polymeric glasses or semicrystalline materials. In addition to these fundamental problems, there may be other problems with the technique, such as the difficulty of sealing a piston without introducing excessive friction.

PVT techniques using confining fluids<sup>7-9</sup> to generate true hydrostatic conditions do not suffer from these systematic errors, since the exact solution of the boundary value problem is used in the calculation of the volume change. PVT techniques using confining fluids must be preferred to the 'piston/die' type of apparatus because of their universal applicability to solids and liquids.

There is another aspect related to this topic. It has become quite common to measure the 'pressure' in polymer injection moulding with transducers placed in cavity walls, sprues, runners, etc. These transducers measure the stress normal to the cavity wall, the  $\sigma_T$  of our discussion. This may or may not be the same as a hydrostatic pressure acting on the material, depending on the nature and physical state of the material (melt, glassy, semicrystalline). This will not limit the use of such transducers in the empirical control of the injection moulding process, where transducer readings are used primarily to establish reproducible conditions, but it would certainly limit their straightforward use for the control of moulding based on actual PVT properties, since the latter are (or should be) based on hydrostatic pressure.

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