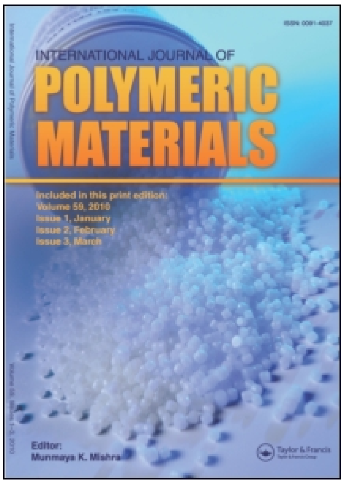

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effect of Pressure on the Mechanical Properties of Polymers. 3. Substitution of the Glassy Parameters for those of the Occupied Volume

W. K. Moonan[a]; N. W. Tschoegl[a]
[a] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California

To cite this Article Moonan, W. K. and Tschoegl, N. W.(1984) 'Effect of Pressure on the Mechanical Properties of Polymers. 3. Substitution of the Glassy Parameters for those of the Occupied Volume', International Journal of Polymeric Materials, 10: 3, 199 — 211

To link to this Article: DOI: 10.1080/00914038408080270

URL: http://dx.doi.org/10.1080/00914038408080270

Intern. J. Polymeric Mater., 1984, Vol. 10, pp. 199–211
0091-4037/84/1003-0199 $18.50/0

Printed in the United Kingdom

Effect of Pressure on the Mechanical Properties of Polymers. 3. Substitution of the Glassy Parameters for those of the Occupied Volume

W. K. MOONAN and N. W. TSCHOEGL

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

(*Received September 27, 1983*)

Replacement of the expansion coefficient and of the bulk modulus and Bridgman constant of the occupied volume by the corresponding parameters of the glass leads to acceptable predictions for the shift factor, a_p, for superposition of stress relaxation measurements as a function of pressure at constant temperature only at low pressures. Various assumptions which are commonly made to obtain free volume parameters from the constants of the WLF equations are examined and their adequacy is assessed.

INTRODUCTION

It was shown in two previous publications[1,2] that the classical free volume theory satisfactorily describes the combined effects of temperature and pressure on shear relaxation in polymeric materials if it is recognized that the bulk modulus depends linearly on pressure. The theory resulting from the inclusion, in the free volume theory, of the proportionality factor, referred to as the Bridgman constant, will be called the FMT theory for brevity. The theory gives the shift distance along the logarithmic time axis required for the superposition of the effects of temperature and pressure as

$$\log a_{TP} = -\frac{c_1^{00}[T-T_0-\theta(P)]}{c_2^{00}(P)+T-T_0-\theta(P)} \tag{1}$$

where T and P are the (absolute) temperature and pressure, respectively, and $\theta(P)$ is given by

$$\theta(P) = c_3^0(P)\ln\left[\frac{1+c_4^0P}{1+c_4^0P_0}\right] - c_5^0(P)\ln\left[\frac{1+c_6^0P}{1+c_6^0P_0}\right]. \tag{2}$$

The quantities c_1–c_6, expressed in terms of the material parameters, are

$$c_1^{00} = B/2.303f_0 \tag{3.1}$$

$$c_2^{00}(P) = f_0/\alpha_f(P) \tag{3.2}$$

$$c_3^0(P) = 1/k_r\alpha_f(P) \tag{3.3}$$

$$c_4^0 = k_r/K_r^* \tag{3.4}$$

$$c_5^0(P) = 1/k_\Phi\alpha_f(P) \tag{3.5}$$

and

$$c_6^0 = k_\Phi/K_\Phi^* \tag{3.6}$$

where the first superscript on the c's refers to the reference temperature, T_0, and the second superscript refers to the reference pressure, P_0. The WLF equation is the special case of the FMT equation when the pressure, P, is the reference pressure, P_0. In this special case the second superscripts may be dropped when P is the atmospheric pressure. The notation then becomes consistent with that of the WLF equation.

In Eqs. (3) B is the proportionality constant well-known from the theory of the WLF equation, f_0 is the fractional free volume at the reference temperature and reference pressure, $\alpha_f(P)$ is the thermal expansion coefficient of the free volume as a function of pressure at the reference temperature, K_r^* is the bulk modulus of the rubber at the reference temperature and zero pressure, k_r, the Bridgman constant, expresses the pressure dependence of the modulus at the reference temperature, and K_Φ^* and k_Φ are the occupied volume analogues of the preceding two quantities. The asterisk refers to zero pressure. The reference pressure, P_0, is 0.1 MPa throughout this paper. The reference temperature, T_0, is 25°C.

The FMT theory can be used to determine all of the free volume parameters if stress relaxation measurements as function of the temperature at constant (atmospheric) pressure are combined with measurements as function of pressure at constant (reference) temperature and, in addition, the thermal expansion coefficient, α_r, and the bulk modulus, K_r^*, and its pressure dependence, k_r, are known at the reference temperature for the material in the rubbery state.

The isothermal stress relaxation measurements as function of pressure yield the expansion coefficient of the occupied volume α_Φ, and its bulk modulus, and the pressure dependence of the later, i.e., K_Φ^* and k_Φ. These relatively costly and difficult measurements could be avoided if the parameters of the material in the glassy state, i.e. α_g, K_g^*, and k_g, could be substituted for those of the occupied volume. Although measurements would still have to be made under pressure, they would be static, i.e. would not need to be made as functions of time. The present paper addresses the question of this substitution.

The expansion coefficient of the occupied volume, α_Φ, has often been replaced in the past[3,4,5] by the expansion coefficient of the glass, α_g, in attempts to determine f_0 from the constants of the WLF equation. Since only two constants, c_1^0 and c_2^0, are available for the determination of B, f_0, and α_f, the assumption that $\alpha_\Phi = \alpha_g$ and consequently, $\alpha_f = \alpha_r - \alpha_g = \Delta\alpha$, allows one to solve for B and f_0 if α_r and α_g have both been determined.

Another procedure consists in solving for f_0/B and α_f/B and assuming that $B = 1$ to obtain an estimate of f_0 and of α_f. Under this assumption $\alpha_f = 1/2.303c_1c_2$. When Assumption 1 is made, it is found[4] that B differs significantly from unity, as is also the case when *no* assumption is made, i.e. α_Φ is obtained from the FMT theory.[2] The values of B and f_0 obtained under Assumption 1 have, however, not been compared so far with the values calculated without making this assumption.

Yet another assumption is possible.[5] Since $\alpha_f = \alpha_r - \alpha_\Phi$, one may simply consider α_Φ to be negligibly small and let $\alpha_\Phi = \alpha_r$. Again, the suitability of this assumption has not been tested.

We have now measured the glassy properties of the materials studied in the two earlier papers in this series[1,2] and are thus in a position to compare the results obtained on the basis of the three assumptions just mentioned with the results furnished by the FMT theory. In addition, we can now answer the questions whether replacement of K_{ϕ}^{*} and k_{ϕ} by K_{g}^{*} and k_{g} furnishes acceptable values for the shift factor, a_{p}, and whether substitution of β_{g}^{*} instead of β_{r}^{*} for β_{ϕ}^{*} leads to reasonable predictions of the WLF-parameters at pressures other than one atmosphere.

MATERIALS

The materials referred to in this paper are Hypalon 40 and Viton B. Their properties, and the preparation of specimens from them, have been discussed before.[1,2]

EXPERIMENTAL PROCEDURE

The extensometer we used to measure the bulk modulus and the expansion coefficient has been described previously.[2] Briefly, changes in the length of a specimen of suitable size and shape are determined using a linear variable differential transformer (LVDT) placed in the pressure vessel in contact with the specimen. The apparatus is calibrated with copper bars of known expansivity. A single measurement of specific volume suffices to convert the length changes to volumes.

The glasses were formed at atmospheric pressure by cooling at the rate of 0.5°C/min. The bulk modulus and its pressure dependence were measured in the pressure apparatus described earlier.[1,2] The high thermal inertia of the apparatus necessitated a different arrangement for measuring the expansion coefficients at atmospheric pressure. For these, the extensometer was placed in a silicone oil bath outside of the pressure apparatus. The oil was cooled at the rate of 0.5°C/min. by flowing liquid nitrogen around the outside of the bath.

RESULTS

Figure 1 shows plots of the specific volumes as functions of temperature at the specified rate of cooling. The solid lines are lines of best

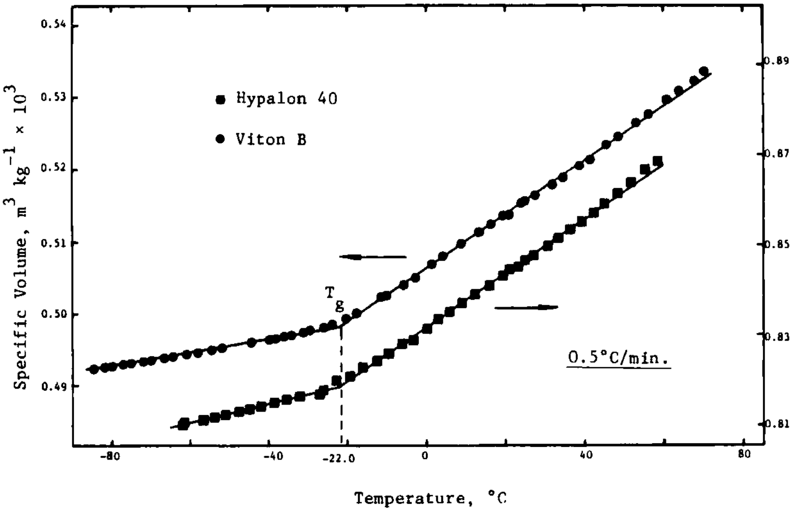

FIGURE 1 Specific volume as a function of temperature for Hypalon 40 and Viton B.

fit. Their slopes yield the expansion coefficients α_r and α_g. These, together with $\Delta\alpha$ and α_f, are tabulated in Table 1. The values of α_r and α_f had, of course, been reported before[2] and are included in Table 1 for ease of comparison. The intersections of the lines in Figure 1 yield the glass transition temperatures, T_g. These happened to be the same, −22.0°C, for both materials. The relations $c_2^g - T_g = c_2^0 - T_0$ and $c_1^g c_2^g = c_1^0 c_2^0$ thus give $c_1^g = 12.21$, $c_2^g = 14.9$°C for Hypalon 40, and $c_1^g = 10.74$, $c_2^g = 13.1$°C for Viton B.

The specific volumes as functions of pressure are tabulated elsewhere.[6] Instead, we show here, in Figure 2, the bulk moduli at zero pressure, $K^*(T)$, as functions of temperature for the two glasses as well as the two rubbers. The latter had again been reported before[2] but are replotted here to illustrate an alternative method which reduces the scatter in $K^*(T)$. In our earlier work, for each temperature at which measurements were made, $K^*(T)$ and k were obtained from fits† to the Murnaghan equation[7]

$$V = V_0\left[\frac{K^*(T)+kP}{K^*(T)+kP_0}\right]^{-1/k}. \tag{4}$$

---

† The measurements were actually obtained in terms of the length, L, and V/V_0 was replaced by $(L/L_0)^3$ in Eq. (4).

Since the values of k showed no discernible trend with pressure, they were averaged and the averages were reported in Table I of Ref. 2. However, neither $K^*(T)$ not k are well determined by a non-linear fit of this kind. We therefore refitted our data to Eq. (4) using the previously determined average value of k. This considerably reduced the scatter in $K^*(T)$ as may be seen by comparing Figure 2 with Figure 3 of Ref. 2. For each material a single point which was clearly an outlier, has been omitted from the new plot.

The glassy data in Figure 2 were treated by the same scatter-reducing procedure. The solid lines represent the Gee equation[8]

$$K^*(T) = K^* \exp -\beta^*(T - T_0) \tag{5}$$

in which β^* is a material parameter governing the temperature dependence of the bulk modulus at zero pressure. The data were, in fact, obtained at atmospheric pressure. However, the difference between atmospheric and zero pressure can be neglected safely. For both materials the Bridgman constants for the glass, k_g, turned out to be indistinguishable within the experimental error from the constants for the rubber, k_r, which are, of course, not affected by the new procedure. Both are entered, therefore, on the same line in Table I where they are also compared with k_ϕ.

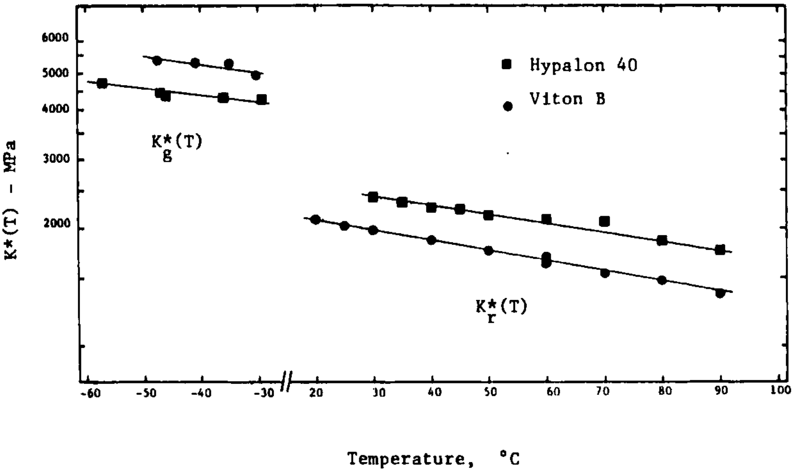

FIGURE 2 The glassy and rubbery bulk moduli of Hypalon 40 and Viton B as functions of temperature.

The new procedure resulted in very slight changes in K_r^* and β_r^*. For Hypalon 40 the new values are 2480 MPa and $5.40\times10^{-3}\,\mathrm{K}^{-1}$. For Viton B they are 2030 MPa and $5.96\times10^{-3}\,\mathrm{K}^{-1}$. These changes do not warrant recalculation of the data and, therefore, the old values are entered in Table I for comparison with K_Φ^* and K_g^*, and with β_g^*.

DISCUSSION

Before turning to the primary subject of this paper we wish to offer some comments regarding the pressure dependence of the bulk moduli since this dependence is a crucial feature of the FMT theory.[2] Our determinations of k_g on Hypalon 40 and on Viton B confirms an observation already made by Simha and coworkers,[9,10] to wit, that k_g and k_r are indistinguishable within the experimental error of the measurement.

Simha *et al.* prefer the Tait equation[2,11,12] to the Murnaghan equation.[7] They write it in the form

$$V = V_0\{1 - C\ln[1 + P/B(T)]\} \tag{6}$$

which is identical with Eq. (5) of Ref. 2 when $P_0 = 0$ and C is substituted for $1/k_t$ and $B(T)$ for $CK_t^*(T)$. The subscript t identifies K_t^* and k_t as parameters of the Tait equation. The latter differs[12] from the Murnaghan equation, Eq. (4), in the reference volume in the definition of the compressibility. According to Tait

$$\kappa_t = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{K_t^* + k_t P}. \tag{7}$$

According to Murnaghan

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{K^* + kP}. \tag{8}$$

The equations obtained by integrating Eqs. (7) and (8) give similar predictions for the volume over a wide range of pressures. It is clearly desirable to be able to interrelate the parameters of the Tait and the Murnaghan equations. Only approximate interrelations can be obtained and these depend on the volume or, equivalently, on the pressure. As shown in the Appendix, we may write

$$K_t^* \simeq K^* V_0/V \quad \text{and} \quad k_t \simeq (k+1)V_0/V. \tag{9}$$

In terms of the notation employed by Simha *et al.* this yields

$$K^*(T) \simeq C^{-1}B(T) \quad \text{and} \quad k \simeq C^{-1} - 1 \tag{10}$$

in the limit of vanishing pressure, i.e. as $V \rightarrow V_0$. Certain cell theories of the liquid state[12,13] predict a pressure dependence of the bulk modulus which is sensibly independent of the structure of the liquid and the temperature. Simha *et al.*[9,10] use a "universal value" of $C = 0.0894$. The latter represents the average of the C-values of several polymers in the glassy as well as in the liquid (melt) state. This value for C is equivalent to a k of 10.19. This agrees extremely well with our experimental values for Hypalon 40 (see Table I) but not quite as well with those for Viton B. The latter disagreement might stem from the filler content (20 phr MT black and 15 phr magnesium dioxide) of our sample of Viton B. This could also explain the fact that, for Viton B, $K_g^* > K_\Phi^*$ while for Hypalon 40 $K_g^* < K_\Phi^*$. If the compressibility of the filler is significantly less than that of the polymer, and the compressibilities are taken to be additive, both K_g^* and K_r^* of the unfilled Viton B would be about 20% lower than the values listed in Table I.

Let us now look at the three assumptions involved in backing out free volume parameters from the c_1 and c_2 values of the WLF

TABLE I

Comparison of material parameters

Parameter	Hypalon 40	Viton B
$\alpha_r \times 10^4\ \mathrm{K}^{-1}$	7.02	7.18
$\alpha_g \times 10^4\ \mathrm{K}^{-1}$	2.51	1.98
$\Delta_\alpha \times 10^4\ \mathrm{K}^{-1}$	4.51	5.20
$\alpha_f \times 10^4\ \mathrm{K}^{-1}$	6.37	5.91
$\beta_r^* \times 10^3\ \mathrm{K}^{-1}$	5.46	6.03
$\beta_g^* \times 10^3\ \mathrm{K}^{-1}$	4.2	4.5
K_r^*, MPa	2510	2040
K_g^*, MPa	3312	3460
K_Φ^*, MPa	3490	3020
k_r, k_g	10.2	14.6
k_Φ	15.8	36.0

TABLE II

B and f_g calculated under various assumptions for α_f

Assumption	Parameter	Hypalon 40	Viton B
None	f_g	0.0095	0.0077
	B	0.267	0.191
$\alpha_f = \Delta\alpha$	f_g	0.0067	0.0070
	B	0.189	0.174
$\alpha_f = 1/2.303\, c_1c_2$	f_g	0.0356	0.0404
	B	1	1
$\alpha_f = \alpha_r$	f_g	0.0105	0.0094
	B	0.294	0.233

equation. The pertinent information is assembled in Table II. Because we have now determined the glass transition temperature, T_g, for Hypalon 40 and Viton B, the fractional free volume is entered as $f_g = f_0 + \alpha_f(T_g - T_0)$. We consider the values obtained from c_1 through c_6 on the basis of the FMT theory to be the best available estimates of the true values of f_0 and B and have entered them in the rows identified as involving no assumption.

We may immediately dismiss Assumption 2 as unrealistic. The f_g-values are much too high, and so are the values for α_f which become $23.9 * 10^{-4}$ for Hypalon 40 and 30.4×10^{-4} for Viton B respectively. This implies that values of f_0 and of α_f calculated on the basis of this assumption[3] are suspect and should not be used in any application where B does not appear as a scaling factor. In fairness it must be pointed out that Assumption 2 may be particularly bad for Hypalon 40 and Viton B which have somewhat unusual WLF constants. (Compare the values given at the end of the first paragraph of the preceding section with the values tabulated by Ferry[3b].)

The f_0 and B values furnished by Assumption 1 look reasonable when compared with those supplied by the FMT theory. This, however, is deceptive. We know of no way to test the value of B. By contrast, the adequacy of the estimate of f_0 obtained on the basis of this assumption can be gauged by using $\Delta\alpha$ instead of α_f in

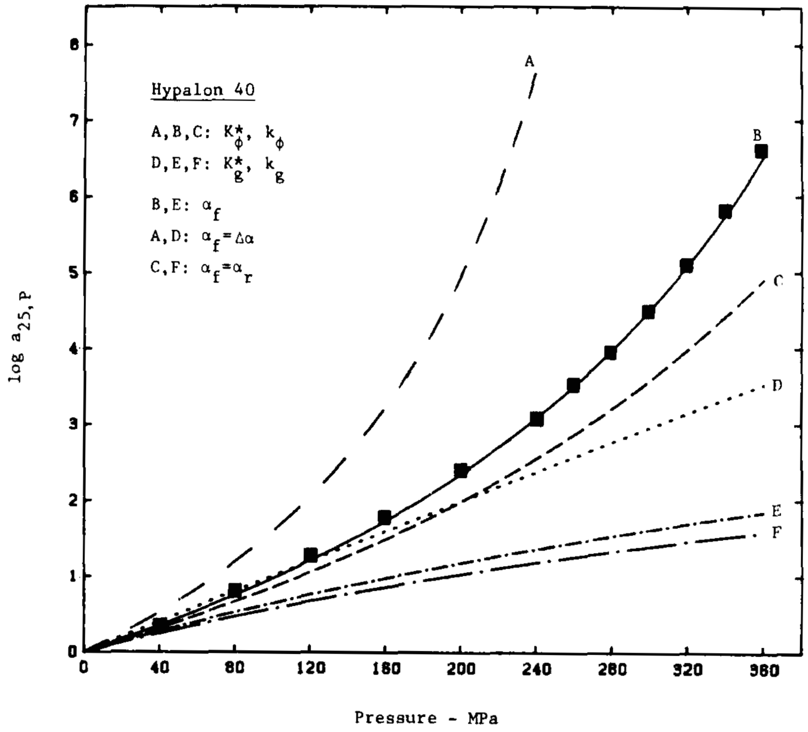

FIGURE 3 The shift distance, $\log a_{25,P}$, for Hypalon 40 as function of pressure under various assumptions.

predicting $\log a_{25,P}$ and comparing that prediction with experimental measurements. $\text{Log}\, a_{25,P}$ is given by Eq. (9) of Ref. 2 in which $f_0 = c_2^{00}(0.1)\ \alpha_f(0.1) \simeq c_2^0 \alpha_f$ so that we have

$$\log a_{25,P} = \frac{c_1^0 \zeta(P)}{c_2^0 \alpha_f k_r - \zeta(P)} \tag{11}$$

where

$$\zeta(P) = \theta(P)/c_3^0(P) = \ln[1 + k_r P/K_r^*] - (k_r/k_\phi)\ln[1 + k_\phi P/K_\phi^*]. \tag{12}$$

The reference pressure, 0.1 MPa, is deemed to be indistinguishable from zero pressure.

The shift distances calculated on the basis of various assumptions are plotted in Figure 3 for Hypalon 40 and in Figure 4 for Viton B. The solid lines, i.e. curves *B*, illustrate the fit of the FMT theory, i.e.

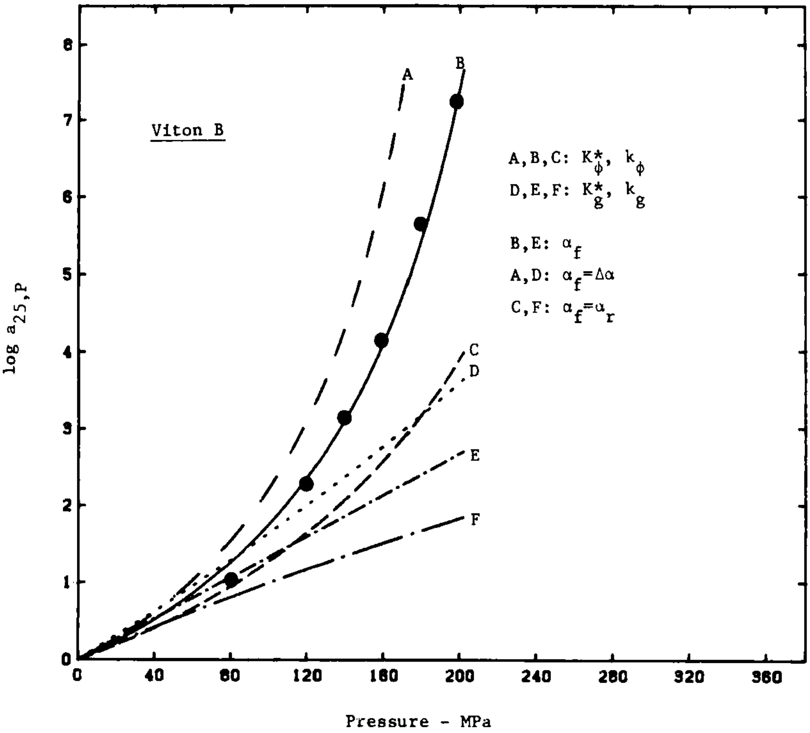

FIGURE 4 The shift distance, log $a_{25,P}$, for Viton B as function of pressure under various assumptions.

Eqs. (11) and (12), to the experimental data. These portions of the figures are reproduced from Figure 4 of Ref. 2 except that the data above the glass transition pressure, P_g, (i.e. above ~200 and 360 MPa, respectively) have been omitted. Curves A and C represent the predictions with $\alpha_f = \Delta\alpha$ (Curve A), and with $\alpha_f = \alpha_r$ (Curve C). At higher pressures Assumption 1, i.e. Curve A, overestimates, and Assumption 3, i.e. Curve C, underestimates the predictions of the FMT-theory. Clearly, however, at higher pressures $\alpha_f = \alpha_r$ gives a better estimate than $\alpha_f = \Delta\alpha$.

Curves E, D, and F again represent predictions with α_f, $\alpha_f = \Delta\alpha$, and $\alpha_f = \alpha_r$, respectively. Now, however, K^*_ϕ and k_ϕ in Eq. (12) have been replaced by K^*_g and k_g. Again $\alpha_f = \Delta\alpha$ (Curve D) overestimates, and $\alpha_f = \alpha_r$ (Curve F) underestimates the predictions obtained with α_f. At higher pressures none of these predictions can be considered to be good ones. Nevertheless, up to a certain pressure (~100 MPa with Viton B and ~140 MPa with Hypalon 40) the shift distances calculated with K_g^*, k_g, and α_g (Curvé D) would be indistinguishable within the experimental error from those obtained with K_Φ^*, k_Φ, and α_Φ. With Hypalon 40 and Viton B the limit of pressure up to which this substitution is acceptable appears to be approximately $P_g/2$.

Of the three parameters K_Φ^*, k_Φ, and α_Φ, it is the Bridgman constant, k_Φ, which has the most pronounced effect at higher pressures. For both materials $k_\Phi > k_r$. This is surprising in view of the empirical relation $k_r = k_g$. Physically it is not easy to see why the bulk modulus of the occupied volume should more strongly depend on pressure than the modulus of either the glass or the rubber.

Finally, a remark is in order concerning β_g^* which we have also determined for both materials (see Table II). We had shown earlier[1,2] that prediction of the WLF constants $c_1^{0P_0}$ and $c_2^{0P_0}$, when the reference pressure is not the atmospheric pressure, requires knowledge of the expansion coefficient of the fractional free volume as a function of pressure, $\alpha_f(P)$, and that this relation can be estimated using Eq. (15) of Ref. 2. Apart from other parameters already discussed, this equation contains β_Φ^* which governs the temperature dependence of the bulk modulus of the occupied volume which we do not know. In principle, β_Φ^* could be obtained from Eq. (5) by making stress relaxation measurements as a function of pressure at different fixed temperatures and backing out $K_\Phi^*(T)$. At the present stage of our technique we consider this futile because of the experimental uncertainties. Attempts to obtain β_Φ^* from measurements as a function of temperature at three different fixed pressures gave inconsistent results. We had shown earlier[2] that substitution of β_r^* for β_Φ^* appears to lead to satisfactory estimates of $\alpha_f(P)$. We now found that the substitution $\beta_\Phi^* = \beta_g^*$ is rather less satisfactory. We suspect that the "true" β_Φ^* would be closer to β_r^* than to β_g^*.

APPENDIX

To derive Eqs. (9) we consider a Taylor–MacLaurin expansion of the volume as a function of pressure. We have

$$V(P) = V_0 + \left.\frac{\partial V(P)}{\partial P}\right|_{P=0} P + \left.\frac{\partial^2 V(P)}{\partial P^2}\right|_{P=0} P^2 + \cdots \qquad \text{(A1)}$$

For the Tait equation this takes the form

$$V(P) = V_0\left[1 - \frac{1}{K_t^*}P + \frac{k_t}{2(K_t^*)^2}P^2 \mp \cdots\right] \tag{A2}$$

while the Murnaghan equation yields

$$V(P) = V_0\left[1 - \frac{V}{V_0K^*}P + \frac{(k+1)V}{2V_0(K^*)^2}P^2 \mp \cdots\right] \tag{A3}$$

Equating coefficients then yields Eqs. (9) as approximate interrelations between the parameters of the Tait and Murnaghan equations.

References

1. R. W. Fillers and N. W. Tschoegl, *Trans. Soc. Rheol.*, **21,** 51 (1977).
2. W. K. Moonan and N. W. Tschoegl, *Macromolecules*, **16,** 55 (1983).
3. J. D. Ferry, *Viscoelastic Properties of Polymers*, (a) 3rd ed., Wiley and Sons, 1980, p. 277; (b) 2nd ed., Wiley and Sons, 1970, p. 316.
4. F. R. Schwarzl and F. Zahradnik, *Rheol. Acta*, **19,** 137 (1980); F. R. Schwarzl, Proc. VIIIth Intern. Congress Rheology, G. Astarita, G. Marrucci, and L. Nicolais, eds., Plenum Press, N.Y., 1980; pp 243.
5. G. C. Berry and T. G. Fox, *Adv. Polymer Sci.*, **5,** 261 (1967).
6. W. K. Moonan, Ph.D. Dissertation, California Institute of Technology, Pasadena, CA 91125, 1983.
7. F. D. Murnaghan, *Finite Deformation of Elastic Solids*, Wiley, New York, 1951; p. 68.
8. G. Gee, *Polymer*, **7,** 177 (1966).
9. R. Simha, P. S. Wilson and O. Olabisi, *Kolloid-Z. u. Z. Polymere* **251,** 402 (1973).
10. A. Quach and R. Simha, J. Appl. Phys. **42,** 4592 (1971).
11. P. Tait, *Physics and Chemistry of the Voyage of H.M. Ship Challenger*, Cambridge University Press, Cambridge, 1900; Vol. II, p. 1.
12. S. C. Sharda and N. W. Tschoegl, *Trans. Soc. Rheol.*, **20,** 261 (1976).
13. V. S. Nanda and R. Simha, *J. Chem. Phys.* **41,** 1884 (1964).
14. J. G. Curro, *J. Chem. Phys.* **56,** 5739 (1972).

ACKNOWLEDGEMENT

This work was supported by a grant from the Department of Energy.