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Effect of Pressure on the Mechanical Properties of Polymers. 2. Expansivity and Compressibility Measurements

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ABSTRACT: Expansivities and compressibilities which had to be estimated in earlier work have been measured. The method by which the parameters of the free volume theory ($B, f_0, \alpha_\phi, K_\phi^*$, and k_ϕ) were calculated from isobaric and isothermal stress relaxation measurements has been refined. The earlier method for predicting the parameters c_1° and c_2° of the WLF equation at higher fixed pressures has been revised.

I. Introduction

Earlier work in this laboratory[1] described stress relaxation measurements under superposed hydrostatic pressure at different temperatures on selected rubberlike materials. This work led to the development of an equation predicting the superposition of the effects of time, temperature, and pressure. The equation, which will be referred to as the Fillers–Moonan–Tschoegl (or FMT) equation for convenience, is based on the free volume concept and comprises the well-known WLF equation[2] as the special case predicting the effect of temperature at constant (atmospheric) pressure.

The FMT equation takes the form

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

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

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

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

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

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

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

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

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

$$c_6^\circ = k_\phi/K_\phi^* \tag{3.6}$$

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. Thus all parameters are dependent on the choice of reference temperature, $c_1^{\circ\circ}$ and $c_2^{\circ\circ}$ are dependent on the choice of reference pressure also, and $c_2^{\circ\circ}$, c_3°, and c_5° depend, in addition, on the experimental pressure, P. Equations 3 differ from eq 40 and 41 in the earlier publication in drawing attention to these dependencies by employing the more explicit notation introduced here. Unless otherwise stated, the reference conditions are T_0 = 25 °C and P_0 = 0.1 MPa. When the temperature dependence is not expressed explicitly, the parameter is referred to the reference temperature. A material parameter referred to *zero* pressure is distinguished by an asterisk. If a parameter is referred to *atmospheric* pressure, it carries no asterisk, subscript, or superscript referring to pressure. In this way the notation is made consistent with that of the WLF equation and the symbols c_1°, c_2°, f_0, and α_f retain their familiar form. In most cases the numerical values of parameters referred to zero and to atmospheric pressure, respectively, differ negligibly, and so we may substitute, e.g., α_r for α_r^*, etc.

In eqs 3 B is a proportionality constant well-known from the theory of the WLF equation,[1,2] 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. Of the seven material parameters appearing in eqs 3, K_r^* and k_r can be measured independently, and they alone determine c_4°. The remaining five experimental quantities, $c_1^{\circ\circ}$, $c_2^{\circ\circ}(P)$, $c_3^\circ(P)$, $c_5^\circ(P)$, and c_6°, can be obtained from the empirical shift distances determined from stress relaxation measurements in the manner to be discussed below. There are thus five known quantities for five unknown ones. By contrast, measurements as a function of temperature alone (i.e., at constant pressure) lead to an underdetermined system because only two known quantities, the c_1° and c_2° parameters of the WLF equation, are available for determining the three unknowns B, f_0, and $\alpha_f = \alpha_f(P_0)$.

In the work reported in the preceding paper, K_r^*, k_r, and α_r had to be estimated or backed out from the data. We

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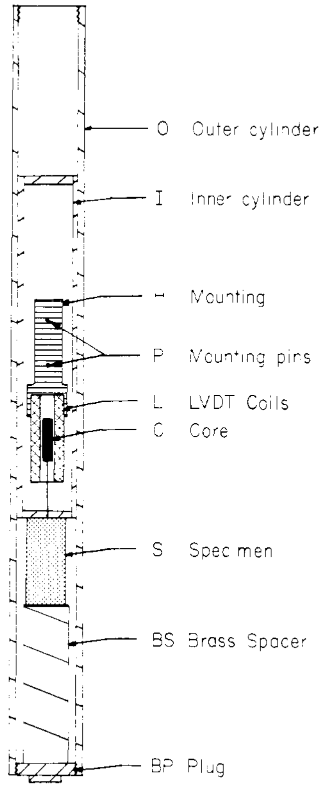

Figure 1. Schematic of extensometer.

have since measured these quantities and have also refined our method for obtaining B, f_0, K_ϕ^*, k_ϕ, and α_f from isobaric and isothermal measurements of the shift distances, log a_{T,P_0} and log $a_{T_0,P}$. In addition, we have revised our earlier method of predicting the WLF parameters at higher fixed pressures. The revision is based on direct measurement of the temperature dependence of the bulk modulus. This paper reports on our reexamination of the validity and utility of the FMT equation in the light of our new measurements and revised procedures.

II. Experimental Section

A. Apparatus. Compressibilities were determined by measuring length changes (multiplied by 3) using a specially constructed extensometer designed to fit into the pressure vessel of the experimental arrangement described in the earlier publication.[1] Pressures were measured with a Heise-Bourdon tube gage with an accuracy of about 1 MPa, with a measuring range from 0 to 160 MPa. The extensometer (see Figure 1) consists of two concentric brass cylinders (I and O), the inner of which (I) is placed on the specimen (S) and moves with it as it changes its length. To minimize friction, contact between the cylinders is limited to six points: three at each end of the inner cylinder. Since the two cylinders tended to stick together when the inner one was raised during an experiment, all runs were made with the inner cylinder moving downward over the course of the experiment. The mass of the inner cylinder is small enough so that compression of the specimen by its weight does not affect the results. The bottom closure plug (BP) supports the specimen and the brass spacer (BS), which can be changed to accommodate specimens of varying length. The inner cylinder is attached to the core (C) of a linear variable differential transformer (L) (Schaevitz Model MHR 100). The LVDT was modified for operation under pressure by drilling holes for pressure relief in its body. The nonmagnetic stainless steel LVDT mounting (H) is connected to the outer cylinder (O) by means of four pins (P). Thus, when the temperature or pressure of the surroundings is changed, the LVDT measures not only the change in length of the specimen but also the motion of the mounting, the LVDT itself, the core, and the outer cylinder.

The LVDT was calibrated at room temperature and atmospheric pressure using a micrometer accurate to 10^{-4} mm. A plot of voltage vs. length from this calibration yields a slope (LVDT gain) and an intercept (voltage output at zero length). At temperatures between 10 and 100 °C and pressures up to 160 MPa the extensometer was calibrated by use of copper bars of varying lengths. The copper was annealed oxygen-free high-conductivity copper whose bulk modulus and coefficient of thermal expansion (145 GPa and 1.62 10^{-5} K^{-1}, both at 25 °C) are small compared to most polymers, thus allowing uncertainties in the properties to be insignificant compared with the expected values of the corresponding properties of the polymer specimens. For temperature calibration, the room-temperature characteristics of the LVDT were used as a base and deviations were recorded for several copper bars as the temperature was lowered from 110 to 10 °C in steps of about 10 °C. The temperature response of the LVDT was linear so that its characteristics can be described by four parameters: the gain and intercept at a fixed temperature and the temperature coefficient of each.

Table I
Measured Material Parameters

parameter	Hypalon 40	Viton B	natural rubber
$\alpha_r \times 10^4$, K^{-1}	7.02 (7.30)	7.18 (6.15)	6.61
K_r^*, MPa	2510 (2000)	2040 (3000)	1690
k_r	10.2 (10.5)	14.6 (12.1)	11.0
$c_4^\circ \times 10^3$, MPa	4.06 (5.25)	7.16 (4.03)	6.51
$\beta_r^* \times 10^3$, K^{-1}	5.46 (1.68)	6.03 (2.83)	3.57
m_r	7.78 (2.3)	8.40 (4.6)	5.40

Calibrations at several pressures up to 160 MPa were made in the same way. The constants determined from the temperature calibration were used as a base. Deviations from the output at atmospheric pressure were recorded as the pressure was increased in steps of 5.3–20 MPa up to a final pressure of 160 MPa. The maximum pressure was deliberately kept low to minimize downtime of the equipment. Although the response of the LVDT to changes in length remained linear at each pressure, the gain and intercept were not linear functions of the pressure. The most convenient way to handle the calibration was to retain the data in tabular form and to interpolate linearly when required.

Thermal expansion coefficients were determined by plotting measured values of the length, L, divided by the reference length, L_0, against temperature. It was found less time-consuming to make these measurements outside the pressure vessel in a separate temperature bath which will be described elsewhere.[4] Full details on the calibration procedure will also be presented elsewhere.[3]

B. Materials. Compressibility and expansivity measurements were made on Hypalon 40 and Viton B, the materials studied earlier.[1] In addition, measurements were made on natural rubber whose expansivity and compressibility have been reported in the literature. These measurements served to check out the experimental procedure.

The first two samples and the preparation of specimens from them were described previously.[1] Natural rubber specimens were prepared using 1.47 parts per hundred parts of rubber (phr) dicumyl peroxide as a cross-linking agent. The sample sheet was cured at 160 °C for 45 min in a laboratory press. On the basis of the work of Lorenz and Parks,[5] we may assume that the efficiency of the cross-linker under these conditions is essentially unity.

The sample sheets were all about 2 mm thick. In order to obtain a specimen of useful thickness, it was necessary to stack 10-mm squares to a height of 20 mm. In the case of natural rubber, where a single piece could be molded, the difference between the thermal expansion coefficient of the stacked pieces and of a single piece was negligible.

III. Results

A. Expansivity Measurements. The volumetric expansion coefficients, α_r, were obtained by multiplying the linear coefficients by 3. Values of α_r for the three rubbers are shown in Table I. The value of α_r reported[6] for natural rubber cross-linked with 3 phr dicumyl peroxide is 6.36 × 10^{-4} K^{-1}. For natural rubber cross-linked with 2% sulfur, a value of 6.61 × 10^{-4} K^{-1} has been found.[7] We conclude

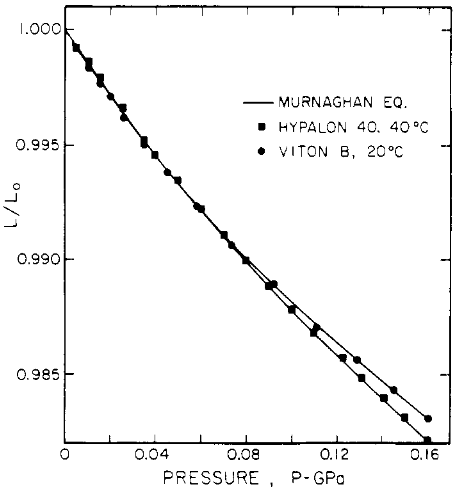

Figure 2. Linear compressibilities of Hypalon 40 and Viton B.

that our value of α_r is accurate within the experimental error.

B. Compressibility Measurements. Compression measurements up to a pressure of 160 MPa were made on the three elastomers at a number of temperatures. Values of L/L_0 vs. pressure were fitted by a nonlinear least-squares procedure to the Murnaghan equation[8] in the form

$$\ln \frac{L}{L_0} = -\frac{1}{3k_r} \ln \left[\frac{K_r^*(T) + k_r P}{K_r^*(T) + k_r P_0} \right] \tag{4}$$

where $K_r^*(T)$ is the zero-pressure bulk modulus at temperature T and k_r is the pressure coefficient of the bulk modulus. The Murnaghan equation describes the length changes of the samples extremely well, as shown, for example, in Figure 2. Values of the Murnaghan constants of natural rubber (see Table I) were in reasonable agreement with those found by Wood and Martin[7] ($K_r^* = 1920$ MPa at 25 °C, $k_r = 11.9$), who fitted their data to the Tait equation.[9] This is expressed in terms of the volume, V, and the reference volume, V_0, as

$$\frac{V - V_0}{V_0} = -\frac{1}{k_r} \ln \left[\frac{K_r^*(T) + k_r P}{K_r^*(T) + k_r P_0} \right] \tag{5}$$

and thus yields somewhat different values of $K_r^*(T)$ and k_r. Full details of the measurements are presented elsewhere.[3] The pressure coefficient k_r varied little and apparently randomly with temperature. Therefore, its values at different temperatures were averaged and these averages were used for the value of k_r at the reference temperature which is required by the analysis to be presented below. The values of $K_r^*(T)$ obtained from the fits to the Murnaghan equation were, in turn, fitted to the equation[10] of Gee

$$K_r^*(T) = K_r^* \exp[-\beta_r^*(T - T_0)] \tag{6}$$

in which β_r^* is a material parameter that governs the temperature dependence of the bulk modulus. Figure 3 shows the data in appropriate coordinates. There is some scatter but the Gee equation seems to hold reasonably well for all three materials. Note that $c_4°$ can now be obtained from eq 3.4. K_r^*, k_r, $c_4°$, and β_r^* are assembled in Table I. The parameter $m_r = \beta_r^*/\alpha_r^*$ will be discussed later.

Table I also contains the earlier, estimated, values of all six parameters for Hypalon 40 and Viton B in parentheses for comparison. The differences are not startling but sufficiently large to affect the values of the material parameters calculated from the shift data. We now turn to these calculations.

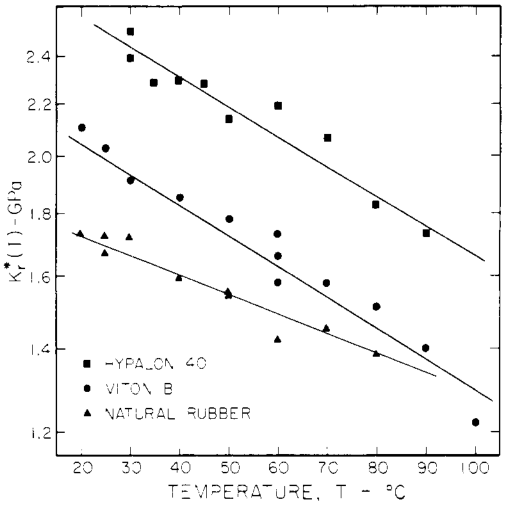

Figure 3. Zero-pressure bulk modulus of Hypalon 40, Viton B, and natural rubber as a function of temperature.

C. Experimental Test of the FMT Equation. To test the validity of eq 1, one may either (1) simultaneously fit data of log $a_{T,P}$ as a function of temperature and pressure to it or (2) utilize the simplified forms that the equation takes under isothermal or isobaric conditions. Method 1 was used to obtain the results presented in the earlier publication.[1] It assumes that $\alpha_f(P) \simeq \alpha_f^*$. This assumption will be discussed in the next section. Method 2 does not require any assumption concerning $\alpha_f(P)$ and is therefore preferable. In this method the isobaric and the isothermal measurements are utilized separately. At the reference pressure $\theta(P)$ vanishes and we recover the WLF equation in the form

$$\log a_{T,P_0} = -\frac{c_1^{\circ\circ}(T - T_0)}{c_2^{\circ\circ} + T - T_0} \tag{7}$$

where $c_2^{\circ\circ} = f_0/\alpha_f(P_0)$. For isobaric measurements at atmospheric pressure, eq 7 reverts to the familiar form, with $c_1°$ and $c_2°$. The parameters $c_1°$ and $c_2°$ are determined from the slope and intercept of the linearized form of the WLF equation.[2] We obtained $c_1° = 2.94$ and $c_2° = 61.9$ °C for Hypalon 40, and $c_1° = 2.34$ and $c_2° = 60.1$ °C for Viton B at atmospheric pressure.

The remaining constants are obtained from isothermal measurements at the reference temperature. For this case, eq 1 becomes

$$\log a_{T_0,P} = \frac{c_1^{\circ\circ}\theta(P)/c_3^{\circ}(P)}{c_2^{\circ\circ}(P)/c_3^{\circ}(P) - \theta(P)/c_3^{\circ}(P)} \tag{8}$$

and $\alpha_f(P)$ scales out. Rewriting eq 8 yields

$$\log a_{T_0,P} = c_1^{\circ\circ}\left\{\ln\left[\frac{1 + c_4^{\circ}P}{1 + c_4^{\circ}P_0}\right] - \frac{k_r}{k_\phi} \ln\left[\frac{1 + k_\phi P/K_\phi^*}{1 + k_\phi P_0/K_\phi^*}\right]\right\} \Bigg/ \left\{f_0 k_r - \ln\left[\frac{1 + c_4^{\circ}P}{1 + c_4^{\circ}P_0}\right] + \frac{k_r}{k_\phi} \ln\left[\frac{1 + k_\phi P/K_\phi^*}{1 + k_\phi P_0/K_\phi^*}\right]\right\} \tag{9}$$

A nonlinear least-squares fit of the isothermal data to eq 9 making use of the known quantities $c_1^{\circ\circ}$, c_4, and k_r (note that $c_2^{\circ\circ}$ is not required) then furnishes the unknowns, f_0, K_ϕ^*, and k_ϕ. The values for Hypalon 40 and Viton B obtained in this way from the shift data of Fillers and Tschoegl[1] are listed in Table II. The excellent fit to eq 9 with these values is shown by the solid lines in Figure

Table II
Calculated Material Parameters

parameter	Hypalon 40	Viton B
B	0.267 (0.230)	0.191 (0.175)
f_0	0.0394 (0.0375)	0.0355 (0.0338)
K_ϕ^*, MPa	3490 (2630)	3020 (6400)
k_ϕ	15.8 (15.1)	36.0 (25.3)
$\kappa_f^* \times 10^4$, MPa^{-1}	1.12 (1.20)	1.59 (1.77)
$\alpha_f \times 10^4$, K^{-1}	6.37 (6.25)	5.91 (5.66)
$\alpha_\phi \times 10^4$, K^{-1}	0.65 (1.05)	1.27 (0.49)

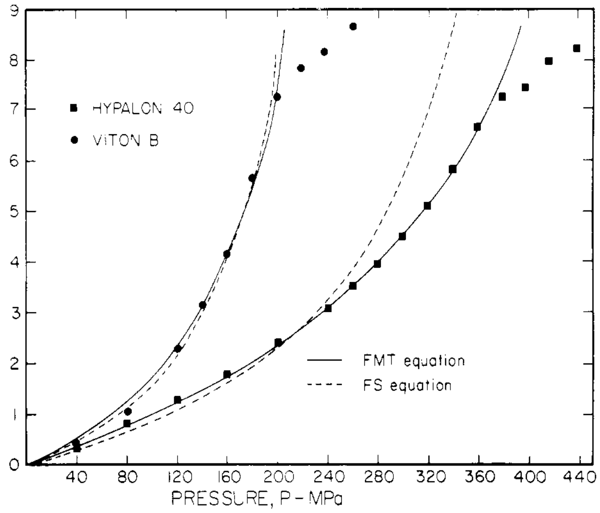

Figure 4. Isothermal shift factors for Hypalon 40 and Viton B.

4. Deviations of the data points from the solid lines mark the onset of glassy behavior.[1] Having found f_0, one next obtains the parameters B and α_f^* from $B = 2.303 f_0 c_1^{oo}$ and $\alpha_f^* \simeq \alpha_f = f_0/c_2^{oo}(0.1 \text{ MPa})$. Finally, the expansivity of the occupied volume is obtained from $\alpha_\phi^* \simeq \alpha_\phi = \alpha_r - \alpha_f$. Numbers in parentheses again represent the values reported earlier.[1] The greatest change is in the values of α_ϕ.

The compressibility of the fractional free volume, which is obtained from

$$\kappa_f^* = (1/K_r^* - 1/K_\phi^*) \tag{10}$$

has also been included in Table II.

D. Isothermal Experiments at Fixed Pressures. With the values of the material parameters in hand, it is possible to predict the behavior of Hypalon 40 and Viton B at high fixed pressures as a function of temperature.[1] At a fixed pressure P_0', different from the pressure P_0 at which the molecular parameters were determined, eq 1 reduces to the WLF equation in the form

$$\log a_{T,P_0'} = -\frac{c_1^{oP_0'}(T - T_0)}{c_2^{oP_0'} + T - T_0} \tag{11}$$

with the constants given by

$$c_1^{oP_0'} = B/2.303 f(T_0,P_0') \tag{12}$$

and

$$c_2^{oP_0'} = f(T_0,P_0')/\alpha_f(P_0') \tag{13}$$

where (see[11] eq 29 of ref 1)

$$f(T_0,P_0') = f_0 - \frac{1}{k_r} \ln\left[\frac{K_r^* + k_r P_0'}{K_r^* + k_r P_0}\right] + \frac{1}{k_\phi} \ln\left[\frac{K_\phi^* + k_\phi P_0'}{K_\phi^* + k_\phi P_0}\right] \tag{14}$$

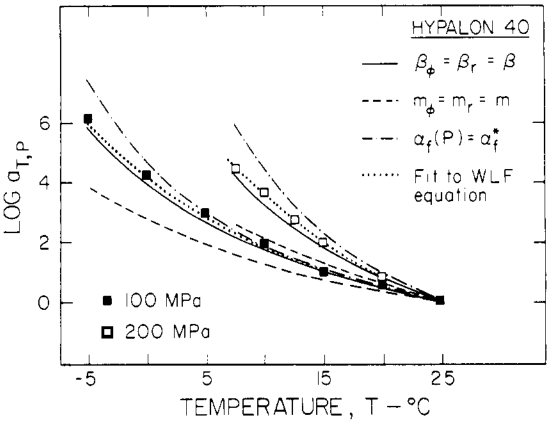

Figure 5. Isobaric shift factors for Hypalon 40 at high pressures.

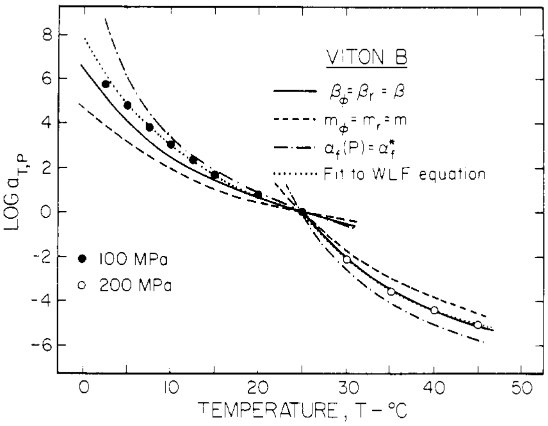

Figure 6. Isobaric shift factors for Viton B at high pressures.

Table III
WLF Parameters at High Pressures

material	pressure, MPa	$c_1^{oP'_0}$	$c_2^{oP'_0}$, °C
Hypalon 40	100	3.91 [5.15]	50.2 [57.2]
	200	5.30 [5.95]	39.0 [40.3]
Viton B	100	4.07 [5.64]	39.9 [42.9]
	200	9.71 [8.99]	18.3 [15.6]

All material parameters are known except $\alpha_f(P')$. By the arguments expounded in the earlier paper (see eq 44–46 there), we write

$$\alpha_f(P_0') = \alpha_f^* - \left[\frac{\beta_r^* P_0'}{K_r^* + k_r P_0'} - \frac{\beta_\phi^* P_0'}{K_\phi^* + k_\phi P_0'}\right] \tag{15}$$

where β_ϕ^* is unknown. The simplest way to cope with this difficulty is to let $\alpha_f(P') = \alpha_f^*$ (case 1). Fillers and Tschoegl[1] had used $\beta_r^* = m_r \alpha_r$ and $\beta_\phi^* = m_\phi \alpha_\phi^*$ and had let $m_\phi = m_r = m$ (case 2). Another procedure is to let $\beta_\phi^* = \beta_r^*$ (case 3).

Figures 5 and 6 compare the experimental shift factors with the predictions offered by all three cases. Clearly, case 3, i.e., $\beta_\phi^* = \beta_r^*$ gives the best results. The agreement is quite remarkable in view of the fact that the material parameters were all derived from independent experiments. Table III shows the WLF parameters predicted for each material at 100 and 200 MPa according to case 3 and compares them with the values (in brackets) obtained from a direct fit according to eq 8. The dotted lines in Figures 5 and 6 represent the fitted WLF equations.

IV. Discussion

Determination of the experimental quantities listed in Table I leaves no adjustable parameter in the FMT theory. The use of α_r, K_r^*, and k_r and application of our revised procedure for calculating the material from the experimental quantities (method 2) have not changed the free volume parameters B, f_0, and α_f dramatically. Larger changes occurred in α_ϕ, K_ϕ^*, and k_ϕ, i.e., in the parameters characterizing the occupied volume.

Determination of the Gee parameter, β_r^*, has led to another revision, namely, that of the procedure for predicting the values of the WLF parameters at fixed higher pressures. The parameter m used in the earlier publication did not survive as a particularly useful concept since direct measurements of β_r^* showed that better agreement is obtained by letting $\beta_\phi^* = \beta_r^*$. For Hypalon 40, $\beta_r^* = 54.6 \times 10^{-4}$ and $m_r\alpha_\phi = 10.7 \times 10^{-4}$. Evidently, $m_r\alpha_\phi$ underestimates β_ϕ^*. We think it likely that β_ϕ^* should be less than β_r^*. Unfortunately, at this time we cannot determine β_ϕ^* directly. It could, of course, be backed out of the data at higher fixed pressures but we defer an examination of this question until we have data on several more polymers.

It must be pointed out that the success of the FMT theory, in both the practical and the theoretical sense, is due entirely to the inclusion of the Bridgman parameters, k_r and k_ϕ. When these are made to vanish, application of l'Hospital's theorem shows that

$$\lim_{k_r,k_\phi \to 0} \theta(P) = (P - P_0)\kappa_f^*/\alpha_f(P) \tag{16}$$

Using eq 16, we find that eq 1 takes the form

$$\log a_{T,P} = -\frac{(B/2.303f_0)[(T - T_0)\alpha_f(P) - (P - P_0)\kappa_f]}{f_0 + (T - T_0)\alpha_f(P) - (P - P_0)\kappa_f} \tag{17}$$

where we have substituted κ_f for κ_f^* for simplicity. The difference between the two quantities should be negligible.

When $P = P_0$ (the isobaric case), we, of course, again recover eq 7. When $T = T_0$, we obtain

$$\log a_{T_0,P} = \frac{c_1{}^{\circ\circ}(P - P_0)}{c_7{}^{\circ\circ} - P + P_0} \tag{18}$$

where $c_7{}^{\circ\circ} = f_0/\kappa_f^* \simeq f_0/\kappa_f$. We now have three known experimental quantities, $c_1{}^{\circ\circ}$, $c_2{}^{\circ\circ}$, and $c_7{}^{\circ\circ}$, to determine four unknown material parameters, B, f_0, α_f, and κ_f. Hence, the system is again underdetermined.

Equation 18 (with $B = 1$) had been proposed by Ferry and Stratton.[12] Its parameters for Hypalon 40 and Viton B are obtained easily; $c_1{}^{\circ\circ}$ is already known from isobaric measurements, and $c_7{}^{\circ\circ}$ may be obtained simply from

$$c_7{}^{\circ\circ} = \sum_{n=1}^{n=N} \frac{1 + c_1{}^{\circ\circ}/\log a_{T_0,P_n}}{N(P_n - P_0)} \tag{19}$$

where N is the number of measurements. This gave $c_7{}^{\circ\circ} = 457$ MPa for Hypalon 40 and $c_7{}^{\circ\circ} = 254$ MPa for Viton B. The Ferry–Stratton (FS) equation with these values is represented by the dashed lines in Figure 4. The FMT equation clearly fits the data better.

Calculating $c_7{}^{\circ\circ}$ from f_0/κ_f^* (see Table II) gives $c_7{}^{\circ\circ} = 352$ MPa for Hypalon 40 and $c_7{}^{\circ\circ} = 223$ MPa for Viton B. However, a fit with these values is worse. The fit of the shift data by the FS equation is much improved if both $c_1{}^{\circ\circ}$ and $c_7{}^{\circ\circ}$ are obtained from the slope and intercept of the linearized form of the equation. Such a fit gives $c_1{}^{\circ\circ} = 5.80$ and $c_7{}^{\circ\circ} = 683$ MPa for Hypalon 40 and $c_1{}^{\circ\circ} = 2.23$ and $c_7{}^{\circ\circ} = 249$ MPa for Viton B. Thus, the FS equation *can* be used to describe the effect of pressure on stress relaxation at the reference temperature. However, it is not possible to gain information from it (either by itself *or* in conjunction with the WLF equation) on the material parameters appearing in the free volume theory. Because the FMT equation contains k_ϕ, the number of unknowns is *one* more than the number of unknowns appearing in a combination of the WLF and the FS equations. However, the *form* of the FMT equation is such that the number of known quantities is increased by *two*.

Equation 18 also fails when one attempts to use it to predict $c_1{}^{\circ P_0'}$ and $c_2{}^{\circ P_0'}$. Equations 12 and 13 are still valid but now

$$f(T_0,P_0') = f_0 - (P_0' - P_0)\kappa_f \tag{20}$$

and

$$\alpha_f(P_0') = \alpha_f^* - (\kappa_r\beta_r^* - \kappa_\phi\beta_\phi^*)P_0' \tag{21}$$

Thus

$$c_1{}^{\circ P_0'} = \frac{c_1{}^{\circ\circ}}{1 - (P_0' - P_0)/c_7{}^{\circ\circ}} \tag{22}$$

and, for case 1, i.e., for $\alpha_f(P_0') = \alpha_f$,

$$c_2{}^{\circ P_0'} = c_2{}^{\circ\circ}[1 - (P_0' - P_0)/c_7{}^{\circ\circ}] \tag{23}$$

For case 3, i.e., for $\beta_\phi^* = \beta_r^*$,

$$c_2{}^{\circ P_0'} = c_2{}^{\circ\circ}\frac{1 - (P_0' - P_0)/c_7{}^{\circ\circ}}{1 - \beta_r^*P_0'c_2{}^{\circ\circ}/c_7{}^{\circ\circ}} \tag{24}$$

For case 2, i.e., for $m_\phi = m_r = m$, we have

$$\alpha_f(P_0') = \alpha_f^*\{1 - mP_0'[\kappa_r - (c_2{}^{\circ\circ}/c_7{}^{\circ\circ})\alpha_\phi]\} \tag{25}$$

The data listed in Tables I and II show that $c_2{}^{\circ\circ}/c_7{}^{\circ\circ}\alpha_\phi$ is about 2 orders of magnitude smaller than κ_r. This term can therefore be neglected. We then find

$$c_2{}^{\circ P_0'} = c_2{}^{\circ\circ}\frac{1 - (P_0' - P_0)/c_7{}^{\circ\circ}}{1 - mP_0'\kappa_r} \tag{26}$$

Plots according to all three cases do not fit the data well. They are shown elsewhere.[3]

V. Concluding Remarks

There is little doubt that the FMT equation is capable of predicting the effect of pressure on stress relaxation in amorphous polymers. Its theoretical value resides in the fact that it allows all the material parameters required by the free volume concept to be determined, at least in principle, from a combination of isobaric and of isothermal measurements. Current work in our laboratory aims at establishing these parameters for a number of elastomers. The results will be reported in another paper in this series.

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Registry No. Hexafluoropropylene–tetrafluoroethylene–vinylidene fluoride copolymer, 25190-89-0.

References and Notes

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