SUPERPOSITION OF THE EFFECTS OF TIME, TEMPERATURE, AND PRESSURE IN POLYMERIC MATERIALS

Thesis by

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to my parents

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ABSTRACT

Stress relaxation was studied in torsion under superposed hydrostatic pressure using a newly constructed device. Combination of these measurements with the determination of expansivities and compressibilities and with earlier measurements of stress relaxation in tension leads to verification of the description of the combined effects of temperature and pressure on shear relaxation by an extension of the classical free volume theory. The predictions of an extension of the Adam-Gibbs theory to the pressure domain are also compared with the data. This theory is not as successful in predicting superposition. The data are also examined in light of an adaptation of the Simha-Somcynsky equation of state to the free volume theory. Prediction of the effect of pressure by the theory requires a single adjustable parameter. It was possible to calculate the free volume parameters of several polymers without use of information from high pressure experiments.

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Chapter 1

INTRODUCTION

Temperature and pressure are two of the most important variables affecting polymer properties. The effect of temperature on the mechanical properties of amorphous polymers has been extensively investigated but relatively little is known about the effect of pressure. High pressures are frequently encountered in the processing of polymers. Studying of the effects of pressure not only aids technological progress but increases our theoretical knowledge as well.

One of the most powerful tools for the investigation and prediction of polymer properties is the concept of time-temperature superposition originally proposed by Leaderman[1] and applied by Tobolsky[2] and Ferry.[3] Application of the principle to experimental measurements on amorphous homopolymers and random copolymers results in a considerable reduction in the amount of information needed to characterize the mechanical behavior of such materials as a function of time and temperature. The equivalence of time and temperature is expressed by the shift factor, a_T, which, at temperatures above the glass transition temperature, T_g, sensibly obeys the equation

$$\log a_T = \frac{c_1^\circ (T - T_\circ)}{c_2^\circ + T - T_\circ} \tag{1}$$

where T a the temperature, $T_\circ$ is the reference temperature, and c_1° and c_2° are constants for a given material which depend on the choice of $T_\circ$.

Williams, Landel, and Ferry[3] (WLF) gave a semi-empirical interpretation to eq. (1) (now known as the WLF equation) in terms of the free volume. This theory is based on the observation by Doolittle[4] that for many materials the viscosity, η, depends on the volume as given by

$$\eta = A\exp(BV_\varphi / V_f), \quad V_\varphi + V_f = V \tag{2}$$

where A and B are constants and V_φ and V_f are the so-called occupied and free volumes which make up the total volume, V. The concept underlying Doolittle's equation is that the rate controlling step for viscous flow is the formation of a void into which a molecule or segment can jump. A theoretical interpretation of Doolittle's equation has been given by Turnbull and Cohen^5 who calculated the rate of diffusion of a hard sphere molecule surrounded by nearest neighbors. The sphere does not move until the free volume reaches a critical value, V^*. The mean diffusion rate can be expressed in the form of the Doolittle equation.

Williams, Landel, and Ferry assumed that the free volume increases with temperature, its expansivity, α_f, remaining constant. Their theory was actually given in terms of the fractional free volume

$$f = V_f / V \approx V_f / V_\varphi . \tag{3}$$

The temperature dependence of f is then

$$f = f_0 + \alpha_f (T - T_0) \tag{4}$$

where f_0 is the fractional free volume at the reference temperature. The WLF equation may then be recovered from this, using the result from the molecular theory of viscoelasticity

$$a_T = \frac{\eta T_0 V}{\eta_0 T V_0} \tag{5}$$

where η_0 is the viscosity at T_0. The parameters of the WLF equation are related to the free volume parameters by

$$c_1^0 = B / 2.303 f_0 \tag{6}$$

and

$$c_2^0 = f_0 / \alpha_f . \tag{7}$$

Unfortunately, the WLF theory does not allow evaluation of the constants B, α_f, and f_0 since there are only two relations between the three parameters. This has led to a number of assumptions about these parameters, which are explained in detail in Chapter 3. These assumptions have little justification; it is clearly desirable to have a sounder basis for arriving at values of the free volume parameters.

There are other approaches for obtaining the shift factor. The "excess entropy" approach[6] is similar to the free volume theory in that another excess quantity is assumed to govern the viscosity. The theory leads to an equation which, with only slight modifications, can be put in the form of the WLF equation. Another entropic approach is that of Adam and Gibbs[7] who base their work on that of Gibbs and DiMarzio[8]. The latter authors argue that the glass transition is a manifestation of an underlying second-order thermodynamic transition which would occur under conditions of infinitely slow cooling. Under such circumstances (which cannot even be approached in the laboratory) the configurational entropy becomes very small at a second-order transition temperature, T_2. The work of Adam and Gibbs was based on calculating the probability of cooperative rearrangements among a group of segments. The resulting equation for the shift factor can again be rearranged to the WLF form without much simplification. It also involves three parameters but one of these, ΔC_p, the difference in heat capacity between the liquid (rubber) and the glass, can be measured independently. It is difficult to evaluate the merits of these theories because the set of equations needed to relate the parameters to measured quantities is generally underdetermined. Furthermore, the consistency of the relations cannot be tested. Adding pressure as an independent variable produces a fully determined set of equations whose consistency can now be probed.

Ferry and Stratton[9] suggested a straightforward analog of the WLF equation for the shift factor at constant temperature, a_p:

$$\log a_p = \frac{c_1^o(P-P_o)}{c_7^o + P - P_o} \tag{8}$$

where the constant c_7^o is the analog of c_2^o. O'Reilly's [10] dielectric measurements on poly(vinyl acetate) at pressures up to 140 MPa suggested that the shift factor could be described by

$$\log a_p = C(P-P_o) \tag{9}$$

where C is a constant. The basis of eq. (9) was discussed by Fillers and Tschoegl.[11] Zosel[13] used the torsion pendulum for measurements on poly(vinyl chloride). The measurements did not extend to a high enough pressure to distinguish between eqs. (8) and (9). However, a careful examination of Zosel's data indicates that they are not truly superposable, probably due to the effects of crystallization. Other high pressure experiments[14,15,16] do not allow verification of eqs. (8) and (9). Havlícek, et al.,[17] have extended the Adam-Gibbs theory to the high pressure domain. Their results, discussed in Chapter 4, have been tested only with Zosel's data.

The theory of Fillers and Tschoegl[11,12], upon which this work is based, is an extension of the free volume theory based on the observation that the pressure dependence of the bulk modulus of polymers (and presumably the occupied volume as well) can be described by Murnaghan's equation[18]

$$V = V_0\left[\frac{K+kP}{K+kP_o}\right]^{-1/k} . \tag{10}$$

where K is the bulk modulus and k is its pressure coefficient. The resulting equation, now called the FMT equation, contains the WLF and Ferry-Stratton equations as special cases and allows unambiguous determination of the free volume parameters. It appears several times in the succeeding chapters and will not be displayed here. Fillers and Tschoegl also constructed an apparatus to measure stress relaxation in tension at high pressures. The materials used, selected for their low glass transition pressures, were commercial products containing some fillers. This complicates interpretation of the results. The experiments confirmed the theory but several issues remained open.

Measurements of the expansivity and compressibility of the materials investigated are needed to complete the verification of the theory. These were not available to Fillers and Tschoegl so that values had to be assumed for them. In Chapter 2, measurements of these parameters are reported. In applying these measurements to the FMT equation it was discovered that Fillers and Tschoegl, in their application, had made an unnecessary assumption, namely, that $\alpha_f(P)$ is a constant. Chapter 2 contains a discussion of this as well as a modification to the assumed temperature dependence of the bulk modulus of the occupied volume. A critical evaluation of the Ferry-Stratton equation is also presented in this chapter.

It is difficult and costly to make the measurements necessary to determine the free volume parameters from the FMT theory. It would be very helpful if any methods could be found to estimate high pressure superposition without recourse to high pressure measurements of mechanical properties. Chapter 3 addresses the question of whether some of the traditional assumptions about the free volume theory are of any value in predicting superposition at high pressures. In particular, the possibility is examined of substituting glassy parameters for those of the occupied volume which are a good deal more difficult to obtain.

Fillers and Tschoegl recognized that tensile relaxation is not the best type of experiment for verification of the FMT equation because volume changes caused by pressurization cannot be separated from those caused by the tensile test itself. This, together with the very limited amount of torsional data in the literature, is sufficient motivation for building a new relaxation apparatus which uses an isochoric deformation such as torsion. Chapter 4 reports on such a device and the applicability of the FMT equation to torsional data. The use of heat capacity data allows a comparison of the FMT theory with the theory of Havlicek, et al. Finally, a method recently appearing in the literature is modified to allow prediction of some of the free volume parameters.

The remainder of this thesis is made up of three manuscripts. There is necessarily a certain amount of repetition in the development of the FMT theory in these chapters. Chapter 2 has been published in *Macromolecules*. Chapter 3 has been accepted for publication in *The International Journal of Polymeric Materials*. Chapter 4 is to be submitted to *The Journal of Polymer Science*.

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Chapter 2

EXPANSIVITY AND COMPRESSIBILITY MEASUREMENTS

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

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

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

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

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

$$c_1^{oo} = B/2.303 f_o \tag{3.1}$$

$$c_2^{oo}(P) = f_o/\alpha_f(P) \tag{3.2}$$

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

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

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

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

where the first superscript on the c's refers to the reference temperature, T_o, and the second superscript refers to the reference pressure, P_o. Thus all parameters are dependent on the choice of reference temperature; c_1^{oo} and c_2^{oo} are dependent on the choice of reference pressure also, and c_2^{oo}, c_3^o, and c_5^o depend, in addition, on the experimental pressure, P. Equation 3 differs from eqs 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_o = 25°C and P_o = 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^o, c_2^o, f_o, 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 eq. 3, B is a proportionality constant well known from the theory of the WLF - equation,[1,2] f_o 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 analogs of the preceding two quantities. Of the seven material parameters appearing in eq. 3, K_r^* and k_r can be measured independently, and they alone determine c_4^o. The remaining five experimental quantities, c_1^{oo}, $c_2^{oo}(P)$, $c_3^o(P)$, $c_5^o(P)$, and c_6^o, 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^o and c_2^o parameters of the WLF-equation, are available for determining the three unknowns, B, f_o, and $\alpha_f = \alpha_f(P_o)$.

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 have since measured these quantities and have also refined our method for obtaining B, f_o, K_ϕ^* and α_f from isobaric and isothermal measurements of the shift distances, $\log a_{T,P_o}$ and $\log a_{T_o,P}$. 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.

Experimental

(A) Apparatus. Compressibilities were determined by measuring length changes (multiplied by three) 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 non-magnetic 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 are 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 versus length from this calibration yields a slope (LVDT gain) and an intercept (voltage output at zero length). At temperatures between 10°C 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°C 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.

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 to 20 MPa up to a final pressure of 160 MPa. The maximum pressure was deliberately kept low to minimize down-time 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_o, 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 be presented elsewhere.[3]

(B) Materials. Compressibility and expansivity measurements were made on Hypalon 40 and Viton B, the materials which had been 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 phr dicumyl peroxide as a crosslinking agent. The sample sheet was cured at 160°C for 45 minutes in a laboratory press. On the basis of the work of Lorenz and Parks[5] we may assume that the efficiency of the crosslinker 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.

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 1. The value of α_r reported[6] for natural rubber crosslinked with 3 phr dicumyl peroxide is 6.36×10^{-4} K^{-1}. For natural rubber crosslinked with 2% sulfur a value of 6.61×10^{-4} K^{-1} has been found.[7] We conclude that our value of α_r is accurate within the experimental error.

Table 1

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
$c_4^o \times 10^3$ [MPa]	4.06 (5.25)	6.16 (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

(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_o versus pressure were fitted by a non-linear least squares procedure to the Murnaghan equation[8] in the form

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

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 1) 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_o, as

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

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

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

in which β_r^* is a material parameter which 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^o can now be obtained from eq. 3.4. K_r^*, k_r, c_4^o, and β_r^* are assembled in Table 1. The parameter $m_r = \beta_r^*/\alpha_r^*$ will be discussed later.

Table 1 also contains the earlier, estimated, values of all six parameters for Hypalon 40 and Viton B in the 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.

(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 which 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 $\alpha_f(P) = \alpha_f^*$. 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

$$\log a_{T,P_o} = -\frac{c_1^{oo}\,(T - T_o)}{c_2^{oo} + T - T_o} \qquad (7)$$

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

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

$$\log a_{T_o,P} = \frac{c_1^{oo}\theta(P)/c_3^o(P)}{c_2^{oo}(P)/c_3^o(P) - \theta(P)/c_3^o(P)} \qquad (8)$$

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

$$\log a_{T_o,P} = c_1^{oo} \frac{\ln\left[\dfrac{1+c_4^oP}{1+c_4^oP_o}\right] - \dfrac{k_r}{k_\phi}\ln\left[\dfrac{1+k_\phi P/K_\phi^*}{1+k_\phi P_o/K_\phi^*}\right]}{f_ok_r - \ln\left[\dfrac{1+c_4^oP}{1+c_4^oP_o}\right] + \dfrac{k_r}{k_\phi}\ln\left[\dfrac{1+k_\phi P/K_\phi^*}{1+k_\phi P_o/K_\phi^*}\right]} \quad . \tag{9}$$

A non-linear least squares fit of the isothermal data to eq. 9 making use of the known quantities c_1^{oo}, c_4, and k_r (note that c_2^{oo} is not required) then furnishes the unknowns, f_o, 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 2. The excellent fit to eq. 9 with these values is shown by the solid lines in Figure 4. Deviations of the data points from the solid lines mark the onset of glassy behavior.[1] Having found f_o, one next obtains the parameters B and α_f^* from $B = 2.303f_oc_1^{oo}$ and $\alpha_f^* \doteq \alpha_f = f_o/c_2^{oo}(0.1\ \text{MPa})$. Finally, the expansivity of the occupied volume is obtained from $\alpha_\phi^* \doteq \alpha_\phi = \alpha_r - \alpha_f$.

Table 2

Calculated Material Parameters

Parameter	Hypalon 40	Viton B
B	0.267 (0.230)	0.191 (0.175)
f_o	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)

Numbers in parentheses again represent the values reported earlier[2]. The greatest change is in the values for α_ϕ.

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

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

has also been included in Table 2.

(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_o', different from the pressure, P_o, at which the molecular parameters were determined, eq. 1 reduces to the WLF equation in the form

$$\log a_{T,P_o'} = -\frac{c_1^{oP_o'}(T - T_o)}{c_2^{oP_o'} + T - T_o} \tag{11}$$

with the constants given by

$$c_1^{oP_o'} = B/2.303f(T_o,P_o') \tag{12}$$

and

$$c_2^{oP_o'} = f(T_o,P_o')/\alpha_f(P_o') \tag{13}$$

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

$$f(T_o,P_o') = f_o - \frac{1}{k_r}\ln\left[\frac{K_r^* + k_r P_o'}{K_r^* + k_r P_o}\right] + \frac{1}{k_\phi}\ln\left[\frac{K_\phi^* + k_\phi P_o'}{K_\phi^* + k_\phi P_o}\right] \quad . \tag{14}$$

All material parameters are known except $\alpha_f(P')$. By the arguments expounded in the earlier paper (see eqs. 44, 45, and 46 there) we write

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

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 3 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.

Table 3

WLF Parameters at High Pressures

Material	Pressure [MPa]	$c_1^{oP'_o}$	$c_2^{oP'_o}$ [°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]

Discussion

Determination of the experimental quantities listed in Table 1 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) has not changed the free volume parameters, B, f_o, 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, $\beta_r^* = 54.6\times10^{-4}$ and $m_r\alpha_\phi = 10.7\times10^{-4}$. *Evidently,* $m_r\alpha_\phi$ *under-estimates* 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, both in 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

$$\lim_{k_r,k_\phi\to o} \theta(P) = (P-P_o)\kappa_f^*/\alpha_f(P) \quad . \qquad (16)$$

Using eq. 16, eq. 1 takes the form

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

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

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

$$\log a_{T_o,P} = \frac{c_1^{oo}(P-P_o)}{c_7^{oo} - P+P_o} \tag{18}$$

where $c_7^{oo} = f_o/\kappa_f^* \doteq f_o/\kappa_f$. We now have three known experimental quantities, c_1^{oo}, c_2^{oo}, and c_7^{oo}, to determine four unknown material parameters, B, f_o, 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^{oo} is already known from isobaric measurements and c_7^{oo} may be obtained simply from

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

where N is the number of measurements. This gave

c_7^{oo} = 457 MPa for Hypalon 40 and c_7^{oo} = 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^{oo} from f_o/κ_f^* (see Table 2) gives c_7^{oo} = 352 MPa for Hypalon 40 and c_7^{oo} = 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^{oo} and c_7^{oo} are obtained from the slope and intercept of the linearized form of the equation. Such a fit gives $c_1^{oo} = 5.80$ and $c_7^{oo} = 683$ MPa for Hypalon 40, and $c_1^{oo} = 2.23$ and $c_7^{oo} = 249$ 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 $c_1^{oP'_o}$ and $c_2^{oP'_o}$. Equations 12 and 13 are still valid but now

$$f(T_o,P'_o) = f_o - (P'_o-P_o)\kappa_f \tag{20}$$

and

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

Thus

$$c_1^{oP'_o} = \frac{c_1^{oo}}{1 - (P'_o-P_o)/c_7^{oo}} \tag{22}$$

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

$$c_2^{oP'_o} = c_2^{oo}[1 - (P'_o-P_o)/c_7^{oo}]. \tag{23}$$

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

$$c_2^{oP'_o} = c_2^{oo} \frac{1 - (P'_o - P_o)/c_7^{oo}}{1 - \beta_r^* P'_o c_2^{oo}/c_7^{oo}} \quad . \tag{24}$$

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

$$\alpha_f(P'_o) = \alpha_f^* \{1 - mP'_o[\kappa_r - (c_2^{oo}/c_7^{oo})\alpha_\phi]\} \quad . \tag{25}$$

The data listed in Tables 1 and 2 show that $c_2^{oo}/c_7^{oo}\alpha_\phi$ is about two orders of magnitude smaller than κ_r. This term can therefore be neglected. We then find

$$c_2^{oP'_o} = c_2^{oo} \frac{1 - (P'_o - P_o)/c_7^{oo}}{1 - mP'_o\kappa_r} \quad . \tag{26}$$

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

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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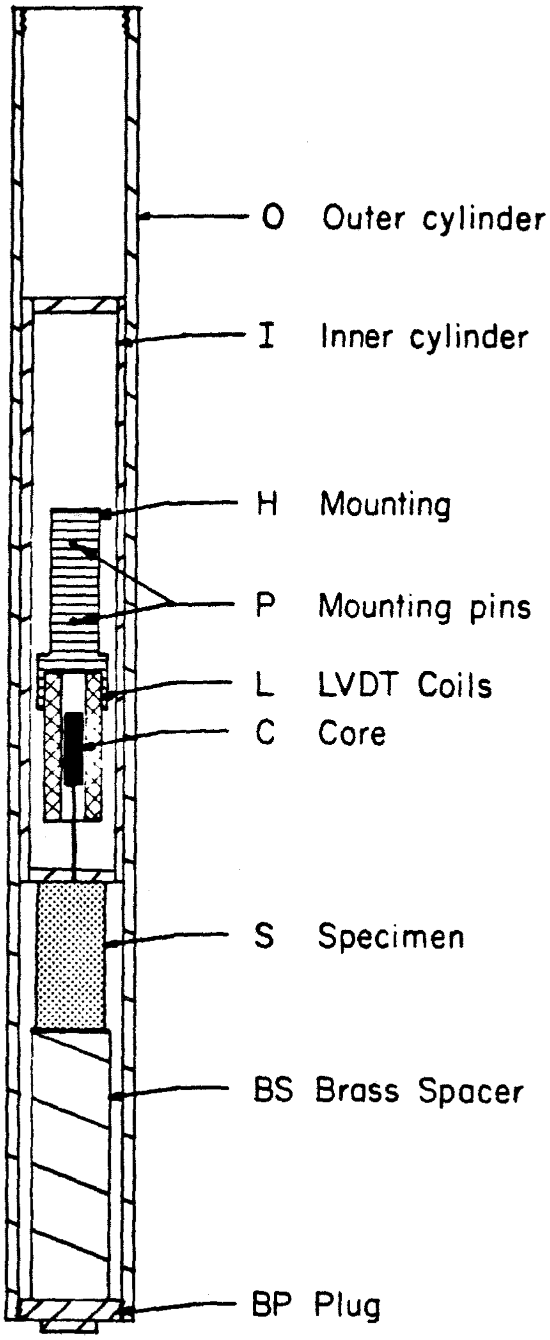

Figure 1, Schematic of Extensometer

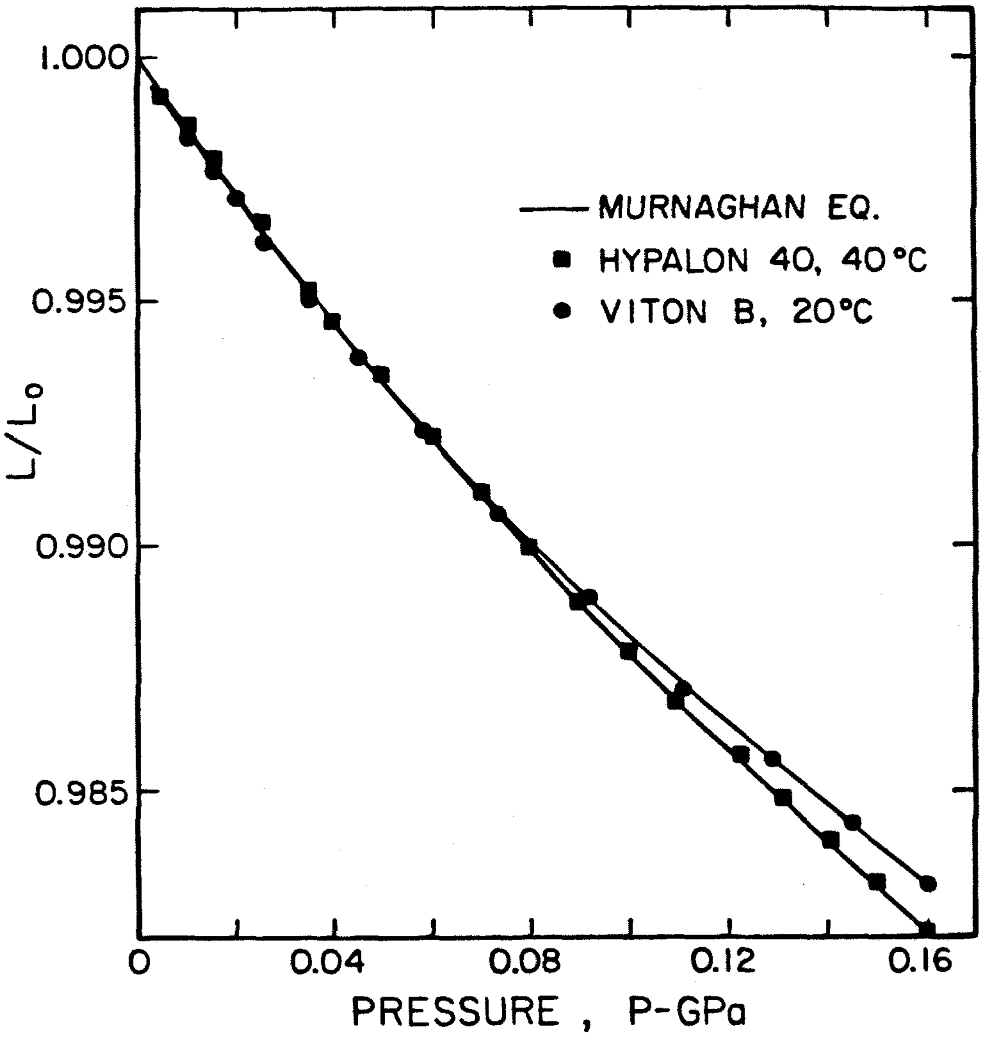

Figure 2. Linear compressibilities of Hypalon 40 and Viton B.

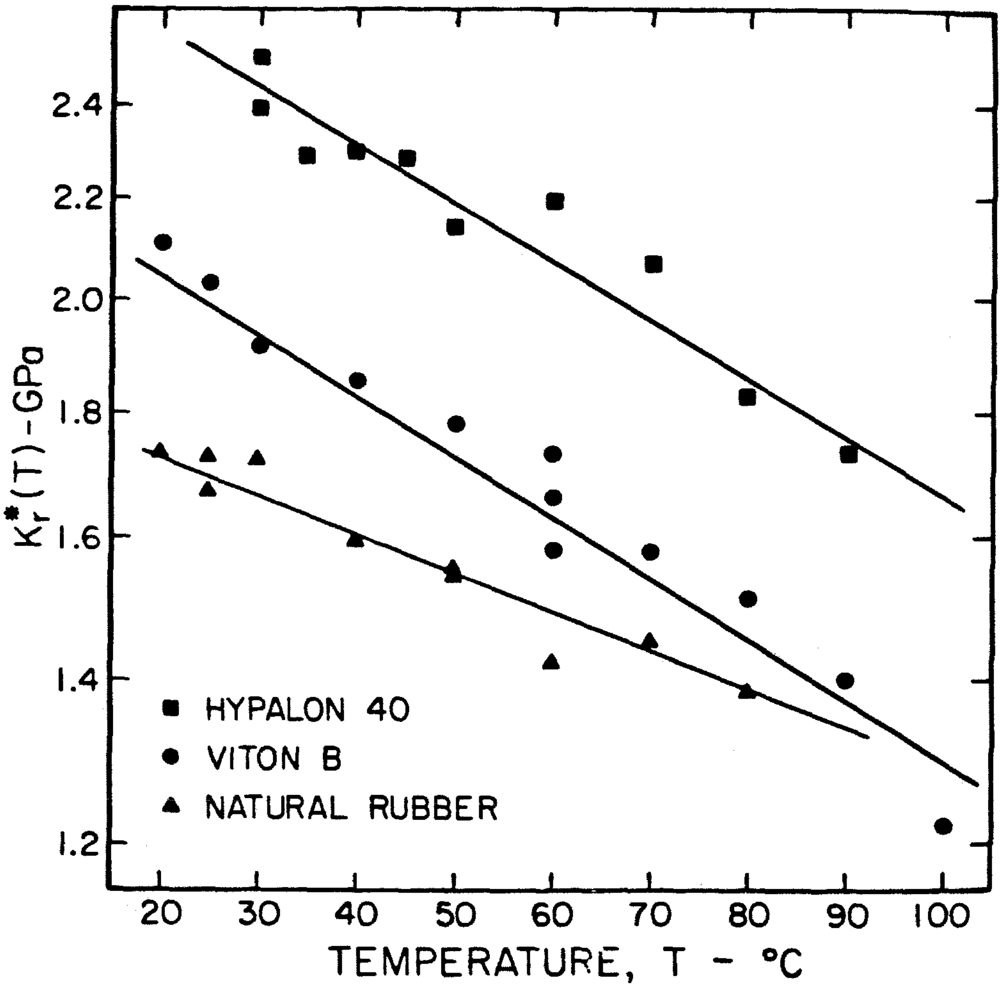

Figure 3. Zero-pressure bulk modulus of Hypalon 40, Viton B, and natural rubber as a function of temperature.

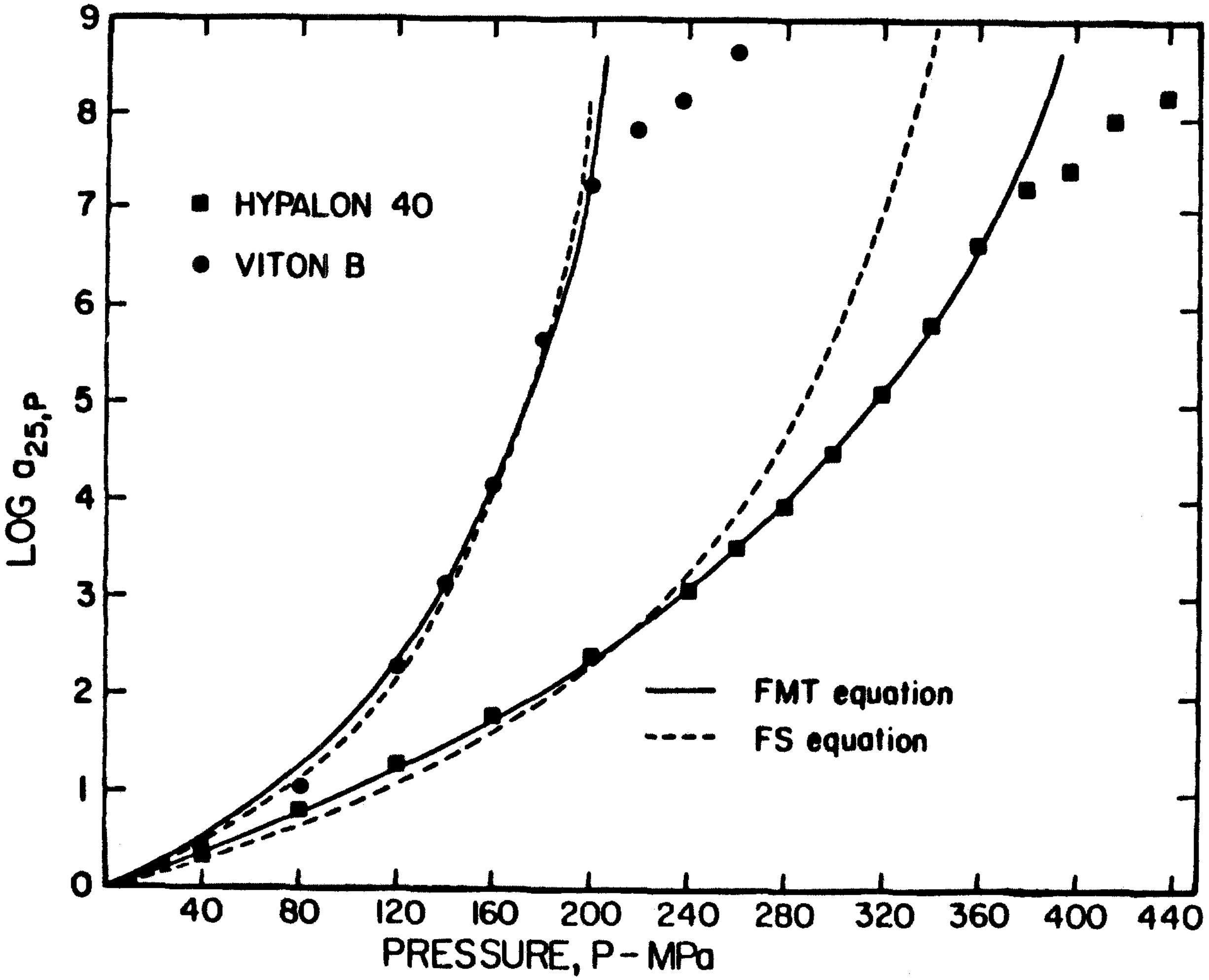

Figure 4. Isothermal shift factors for Hypalon 40 and Viton B.

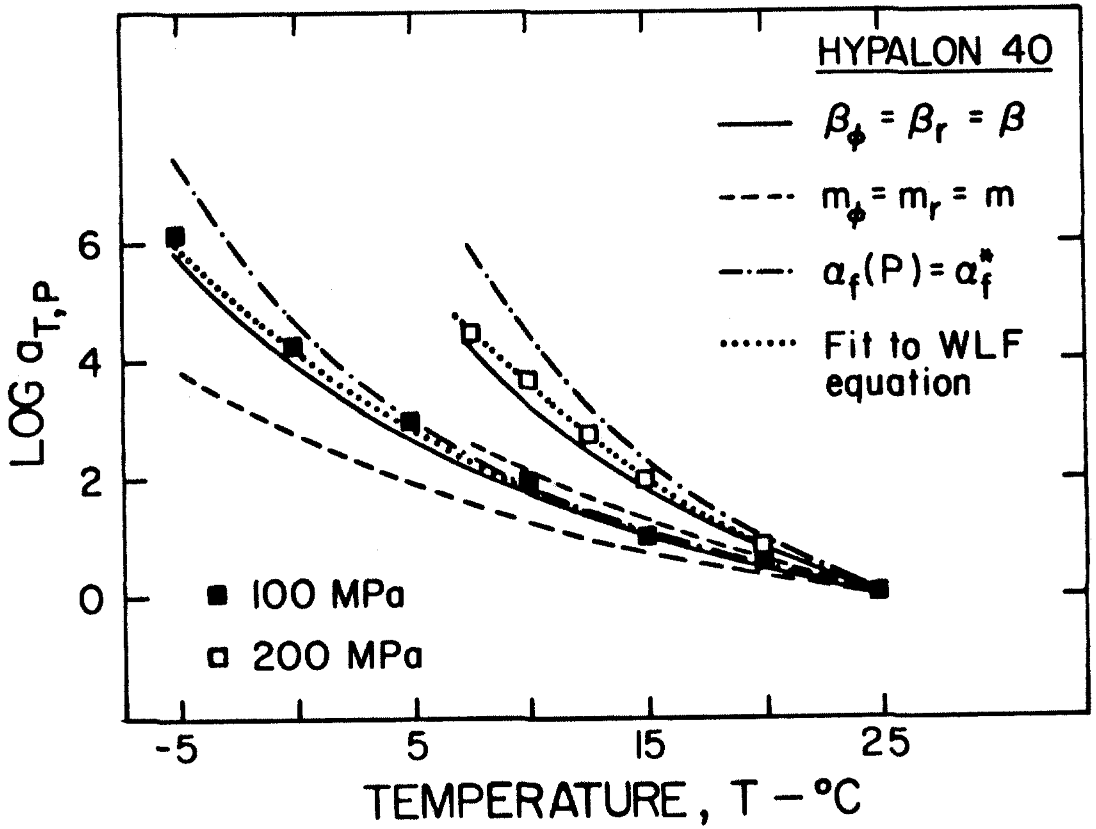

Figure 5. Isobaric shift factors for Hypalon 40 at high pressures.

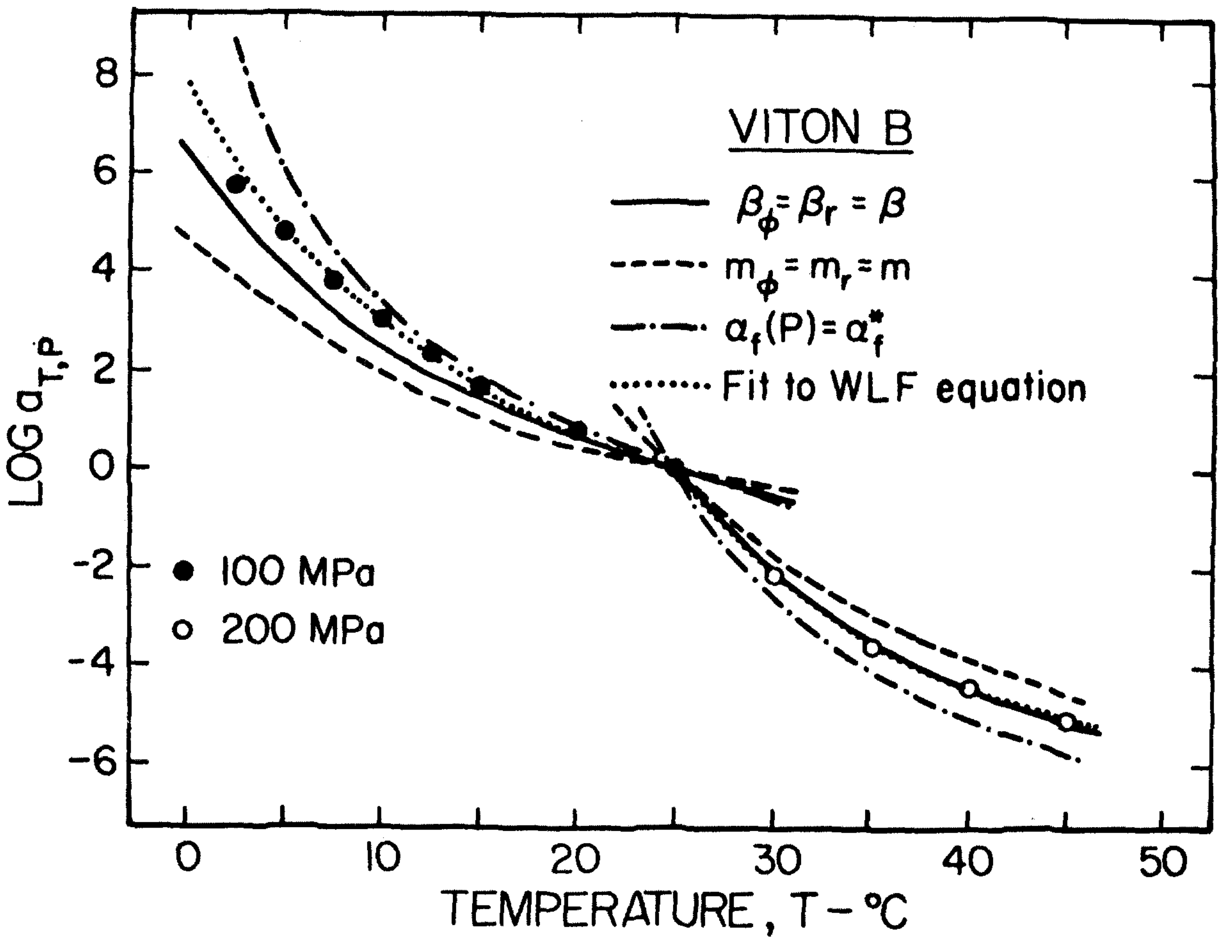

Figure 6. Isobaric shift factors for Viton B at high pressures.

Chapter 3

SUBSTITUTION OF GLASSY PARAMETERS FOR THOSE OF THE OCCUPIED VOLUME

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

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

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

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

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

$$c_1^{oo} = B/2.303f_o \tag{3.1}$$

$$c_2^{oo}(P) = f_o/a_f(P) \tag{3.2}$$

$$c_3^{o}(P) = 1/k_r a_f(P) \tag{3.3}$$

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

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

and

$$c_6^{o} = k_\phi / K_\phi^* \qquad (3.6)$$

where the first superscript on the c's refers to the reference temperature, T_o, and the second superscript refers to the reference pressure, P_o. The WLF equation is the special case of the FMT equation when the pressure, P, is the reference pressure, P_o. 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_o 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_o, is 0.1 MPa throughout this paper.

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 a 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 a function of pressure yield the expansion coefficient of the occupied volume, α_ϕ , and its bulk modulus, and the pressure dependence of the latter, 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_o from the constants of the WLF equation. Since only two constants, c_1^o and c_2^o, are available for the determination of B, f_o, 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_o if α_r and α_g have both been determined.

Another procedure consists in solving for f_o/B and α_f/B and assuming that B=1 to obtain an estimate of f_o 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_o obtained under Assumption 1 have, not, however, 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_{T}^{*} 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 speciments 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 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 $c_2^g - T_g = c_2^o - T_o$ and $c_1^g\ c_2^g = c_1^o\ c_2^o$ 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*

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

to the Murnaghan equation[7]

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

Since the values of k showed no discernible trend with pressure, they were averaged and the averages were reported in Table I of Reference 2. However, neither K*(T) nor k is 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 Reference 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]

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

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, of course, are not affected by the new procedure. Both are entered, therefore, on the same line in Table 1 where they are also compared with k_ϕ.

The new procedure resulted in very slight changes in K^*_r and β^*_r. For Hypalon 40 the new values are 2480 MPa and $5.40 \times 10^{-3}\ K^{-1}$. For Viton B they are 2030 MPa and $5.96 \times 10^{-3}\ K^{-1}$. These changes do not warrant recalculation of the data and, therefore, the old values are entered in Table 1 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 confirm 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

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

which is identical with Eq. (5) of Reference 2 when $P_o=0$ 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

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

According to Murnaghan

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

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

$$K_t^* = K^*V_o/V \quad \text{and} \quad k_t = (k+1)V_o/V \ . \qquad (9)$$

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

$$K^*(T) = C^{-1}\,B(T) \quad \text{and} \quad k = C^{-1} - 1 \qquad (10)$$

in the limit of vanishing pressure, i.e., as $V \to V_o$. 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 1) 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 1.

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 equation. The pertinent information is assembled in Table 2. Because we have now determined the glass transition temperature, T_g, for Hypalon 40 and Viton B, the fractional free volume is entered as $f_g = f_o + \alpha_f (T_g - T_o)$. 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_o 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_o 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_o 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_o obtained on the basis of this assumption can be gauged by using $\Delta\alpha$ instead of α_f in predicting log $a_{25,P}$ and comparing that prediction with experimental measurements. Log $a_{25,P}$ is given by Eq. (9) of Reference 2 in which $f_o = c_2^{oo}(0.1)\ \alpha_f(0.1) = c_2^o\alpha_f$ so that we have

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

where

$$\zeta(P) = \theta(P)/c_3^o(P) = \ln[1 + k_r P/K_r^*(25°)] - (k_r/k_\phi)\ \ln[1 + k_\phi P/K_\phi^*(25°)]. \tag{12}$$

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., Eqs. (11) and (12), to the experimental data. These portions of the figures are reproduced from Figure 4 of Reference 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 (Curve D) would be indistinguishable within the experimental error from those obtained with K^*_ϕ, k_g, 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 2). We had shown earlier[1,2] that prediction of the WLF constants $c_1^{oP_o}$ and $c_2^{oP_o}$, when the reference pressure is not the atmospheric pressure, requires knowledge of the expansion coefficent of the fractional free volume as a function of pressure, $\alpha_f(P)$, and that this relation can be estimated using Eq. (15) of Reference 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.

TABLE 1

Comparison of Material Parameters

Parameter	Hypalon 40	Viton B
$\alpha_r \times 10^4\ K^{-1}$	7.02	7.18
$\alpha_g \times 10^4\ K^{-1}$	2.51	1.98
$\Delta_\alpha \times 10^4\ K^{-1}$	4.51	5.20
$\alpha_f \times 10^4\ K^{-1}$	6.37	5.91
$\beta^*_r \times 10^3\ K^{-1}$	5.46	6.03
$\beta^*_g \times 10^3\ K^{-1}$	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 2

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

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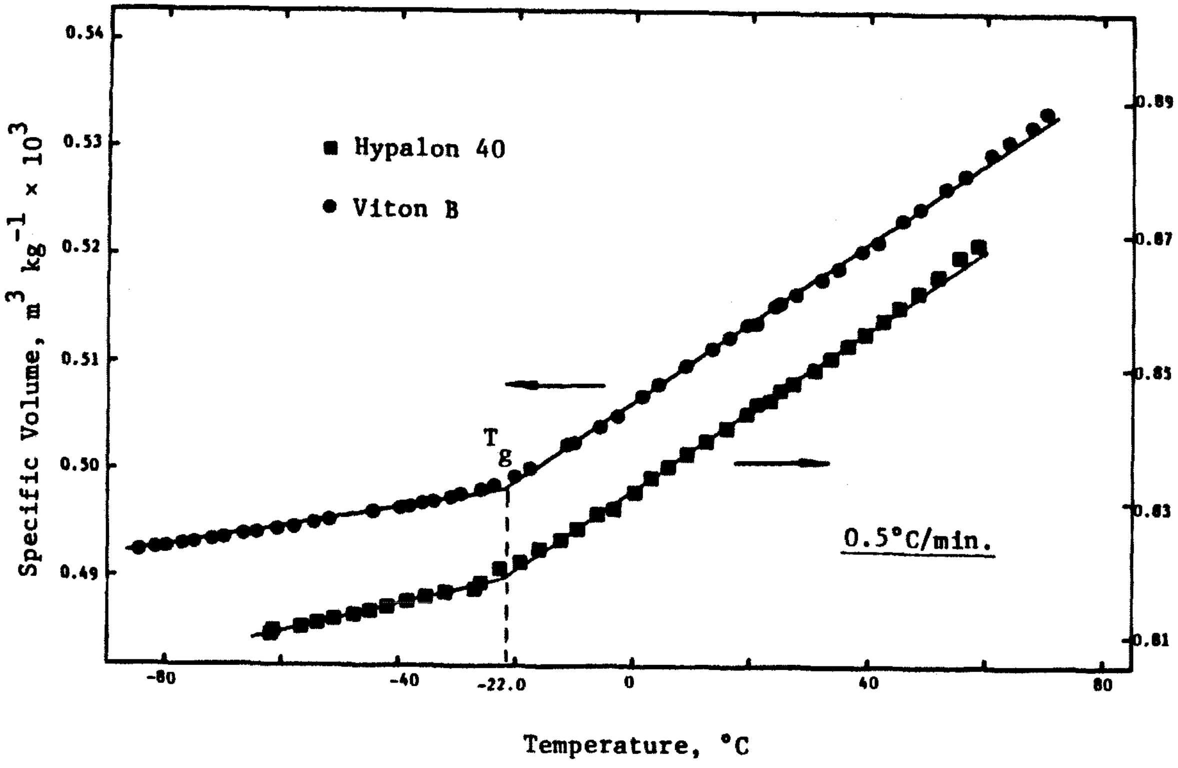

Figure 1 Specific volume as a function of temperature for Hypalon 40 and Viton B.

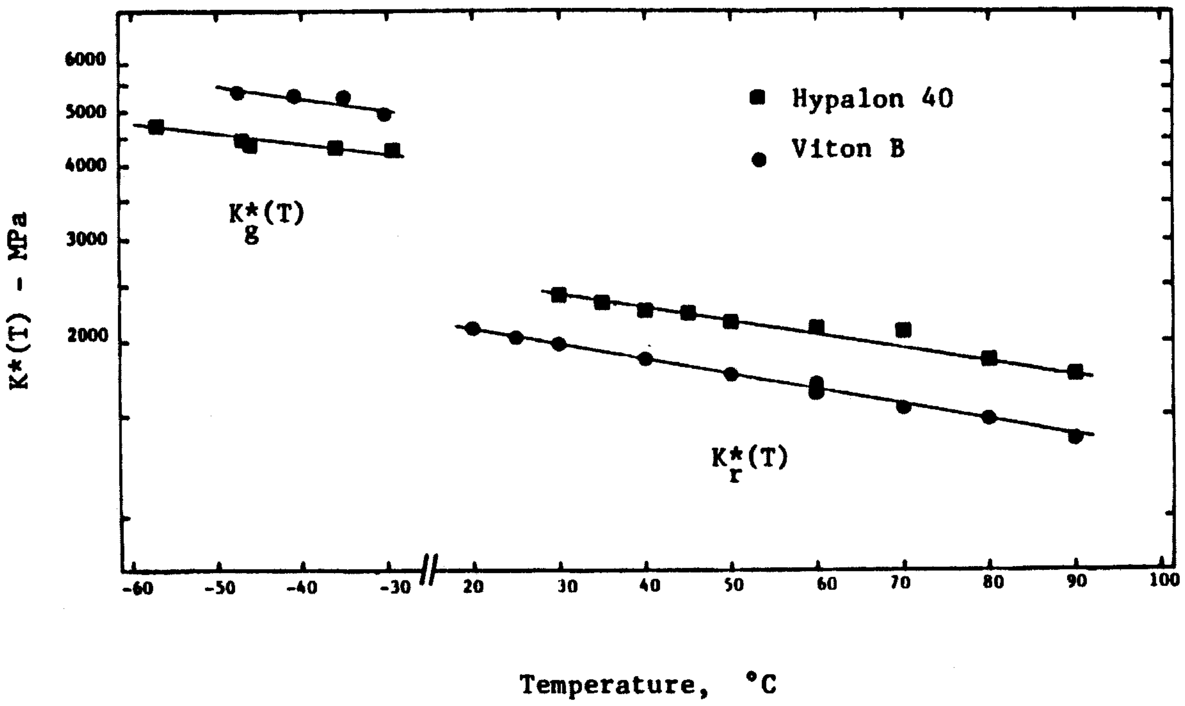

Figure 2 The glassy and rubbery bulk modulii of Hypalon 40 and Viton B as a function of temperature.

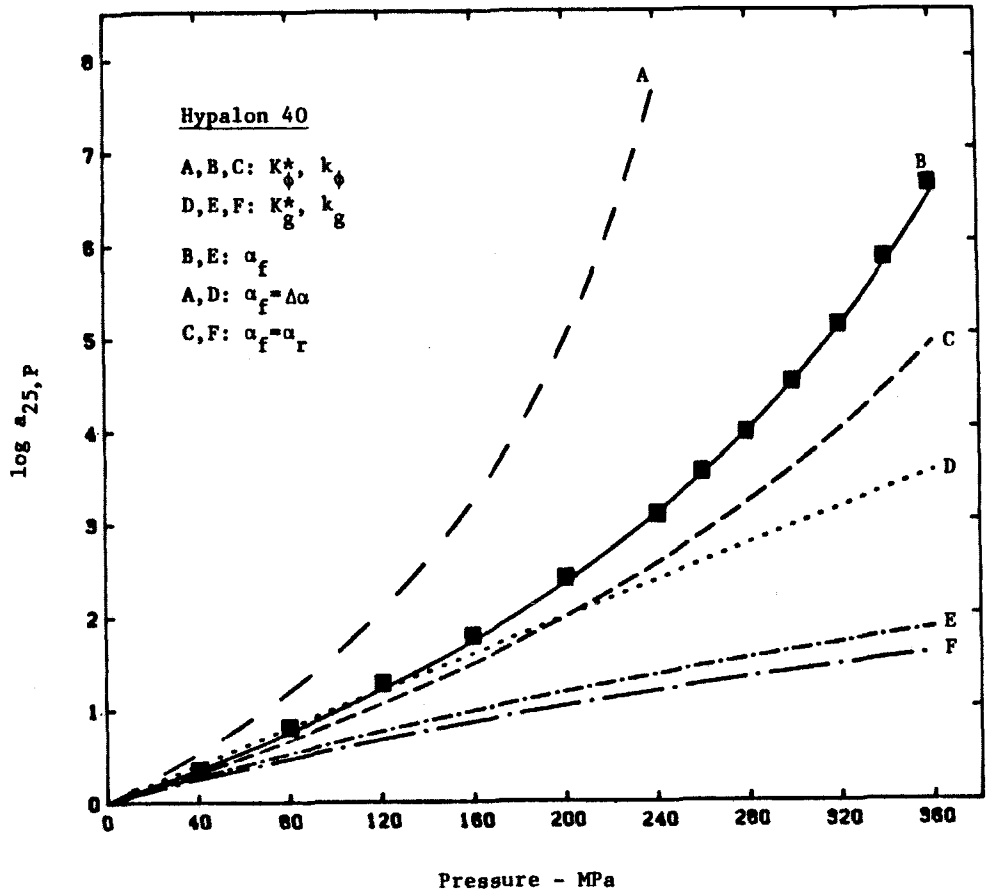

Figure 3 The shift distance, $\log a_{T_0,P}$, for Hypalon 40 as a function of pressure under various assumptions.

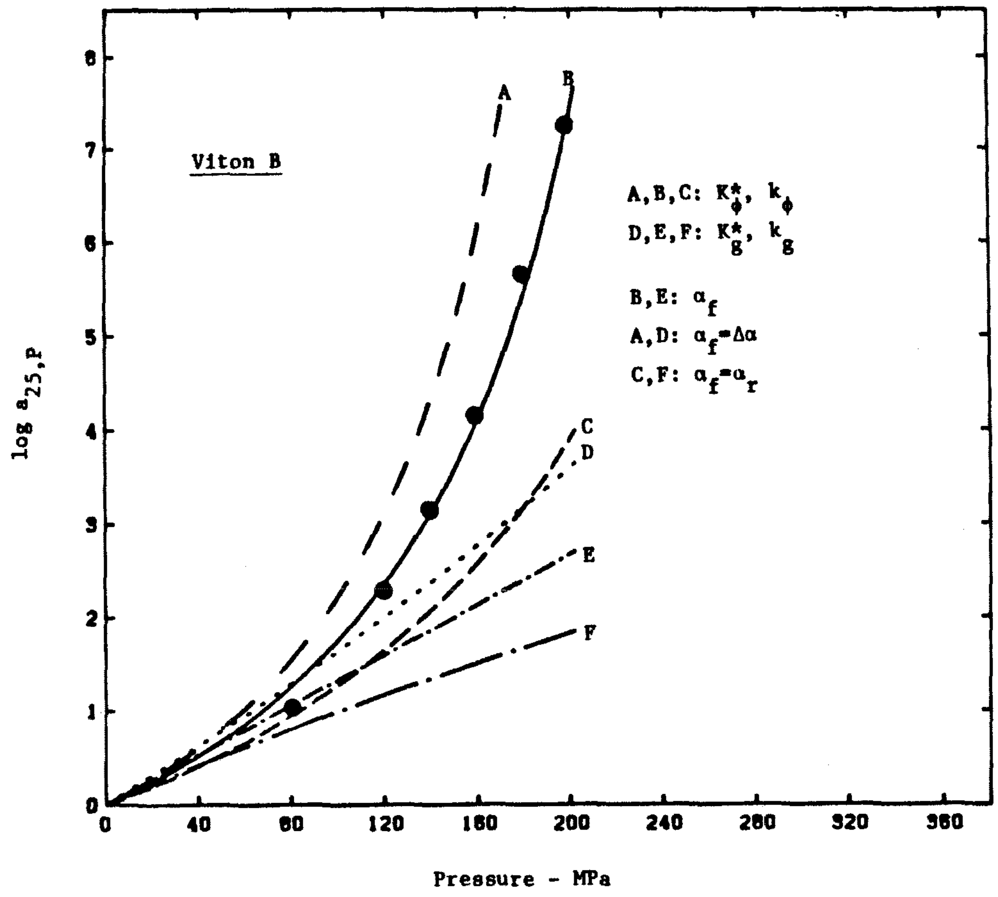

Figure 4 The shift distance, log $a_{T_0,P}$, for Viton B as a function of pressure under various assumptions.

Chapter 4

MEASUREMENTS IN TORSION

INTRODUCTION

In the previous parts of this series[1,2,3] an equation, referred to as the FMT equation for convenience, was developed. This equation, based on the free volume theory, describes time-temperature-pressure superposition of stress relaxation data under superposed hydrostatic pressure. The equation takes the form

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

where T and P are the temperature and pressure, respectively, and

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

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

$$c_1^{oo} = B/2.303 f_o \tag{3.1}$$
$$c_2^{oo}(P) = f_o/\alpha_f(P) \tag{3.2}$$
$$c_3^o(P) = 1/k_T \alpha_f(P) \tag{3.3}$$
$$c_4^o = k_T / K_T^* \tag{3.4}$$
$$c_5^o(P) = 1/k_\varphi \alpha_f(P) \tag{3.5}$$

and

$$c_6^o = k_\varphi / K_\varphi^* \tag{3.6}$$

where the first superscript on the c's refers to the reference temperature, T_o, and the second superscript refers to the reference pressure, P_o. In addition to dependencies on the reference conditions, c_2^{oo}, c_3^o, and c_4^o depend on the experimental pressure, P. When the temperature dependence is not expressed explicitly, the parameter is referred to the reference temperature. A material parameter referred to zero pressure is denoted by an asterisk. A parameter referred to atmospheric pressure carries no reference to pressure so that the familiar WLF symbols, e.g., c_1^o, c_2^o, f_o, and α_f, retain their familiar form. In most cases the numerical values of parameters referred to zero and atmospheric pressure differ negligibly.

In eqs. (3) the parameter B is a proportionality constant well known from the free volume theory[1,4], f_o is the fractional free volume at the reference temperature and reference pressure, $\alpha_f(P)$ is the pressure-dependent thermal expansion coefficient of the free volume, K_T^* is the bulk modulus of the rubber at the reference temperature and zero pressure, k_T is the pressure coefficient of the bulk modulus, and K_φ^* and k_φ are the occupied volume analogs of the preceding two quantities. It has already been shown[2] that the material parameters appearing in eqs. (3) can be determined using superposable sets of relaxation data at the reference pressure, a second set at the reference temperature, and one additional assumption.

In the first paper in this series[1] Fillers and Tschoegl reported measurements of stress relaxation in simple tension under superposed hydrostatic pressure and analyzed the validity of the theory in light of these data. Some of the material properties needed for this test were unavailable at the time and had to be estimated. In the second paper[2], measurements of these material properties were provided and the theory was modified somewhat to account for the results of these measurements. Recently[3], the substitution of certain parameters of the glassy state for those of the occupied volume was discussed. The present paper reports on a new apparatus for measuring stress relaxation in torsion at high pressures and discusses the theory in light of data from this device. Further, other recently proposed descriptions of time-temperature-pressure superposition are discussed.

There are several reasons for constructing an apparatus to measure stress relaxation in torsion. The original measurements[1] of stress relaxation in tension at high pressure are confounded by the fact that the tensile modulus, $E(t)$, represents both changes in shape (distortion) and changes in size (compression). (See eq. (7) and the discussion following it.) The shear modulus, $G(t)$, represents material response to an isochoric (no change in size) deformation and is thus in a sense a more fundamental quantity than the tensile modulus. It is desirable to verify that the theory does describe isochoric stress relaxation.

A second motivation for building this apparatus is to check some inconsistencies in the original measurements. In superposing the earlier tensile stress relaxation data, it was necessary to impose small but systematic shifts of the values of $\log E(t)$ in order to obtain complete superposition of the data. These corrections were required not only at high pressures but also at atmospheric pressure. The shifts were not arbitrary but could only be chosen from a very small range. It was not clear whether the shifts were caused by a defect of the apparatus or experimental procedure or whether they represented a fundamental failure of the time-temperature superposition principle. The latter suggestion is entertained because the measurements were performed in a liquid bath under very precise temperature control, unlike most other laboratory experiments of this kind which are generally performed in gaseous thermostats. Hence these experiments are considered to be a better test of the principle than most other experiments.

A final motivation for the new apparatus is to improve upon the original tensile device which suffered from certain limitations. In particular, its pressure range was too limited for general use and it had to be manually reset after each experiment. This required depressurization of the bomb and a considerable delay afterwards to wait for reestablishment of equilibrium following repressurization. In addition, triggering of the device was unreliable at high pressures. Changes in specimen length at high pressures and low temperatures could not be accurately accounted for. It was hoped that performance could be improved substantially with the new device.

In addition to constructing a new stress relaxation device, the experiments were to be performed on well-characterized, unfilled samples. The original tensile relaxation experiments were performed on filled rubber samples. Although one, Hypalon 40, was only lightly filled, it could not be stated definitely that the FMT equation describes the behavior of unfilled materials.

APPARATUS

The high pressure bomb and pressure generating system have been described previously.[1] Briefly, the bomb is a beryllium copper cylinder with an outer diameter of 152 mm and a length of 350 mm. The interior chamber has a diameter of 23.8 mm and a length of 305 mm. One end of the chamber is connected to the high pressure pumps by means of standard cone fittings. The other end is closed by a removable seal which allows insertion of the core devices within the chamber and also carries three electrical leads. A fourth (common) electrical connection is made through the bomb itself. High pressures (up to 650 MPa) are generated by hand pumps. The pressurizing medium is Dow Corning 200 Silicone Fluid of 5 cs viscosity. The pressure is measured by a strain gauge sensor connected to an Autoclave Engineers DPS-1001 digital pressure indicator, accurate to 0.1 MPa. The sensor was regularly checked against a Heise-Bourdon gauge at 110 MPa.

The bomb is immersed in a tank containing silicone fluid of about 10 cs viscosity. The stirred fluid was cooled to 1°C by a portable immersion cooler (Neslab PBC-2) the probe of which was immersed in the tank. Below 1°C a more powerful cooler (Flexicool FC-100) was used. The lowest temperature reached was -65°C. The temperature was controlled through a proportional integral controller with heating wires. Over the course of a typical relaxation experiment (about 30 minutes) the temperature change was about 0.05°C. The pressure change was too small to be measured.

The bomb accepts three core devices: (1) the tensile relaxometer used in earlier experiments,[1] (2) an extensometer, described previously,[2] used to measure thermal expansion and bulk modulus, and (3) the new torsional relaxometer, shown in Figure 1.

The relaxometer consists of three main parts: a motor (M) for twisting the specimen, a lower frame (LF) to support the specimen and torque measuring cell, and an upper frame (UF) to support a mechanism for control of the angle of twist. The motor must have two characteristics: it must have a relatively high starting torque to provide a good approximation to a step function of strain, and it must have no preferred rotor position which could interfere with the zero deflection adjustment. The Escap motor (model 23-D-21-213E, Portescap U.S.) was selected because its ironless rotor allows it to meet these criteria. The motor shaft turns the upper grip (UG) which is end-bonded to the specimen (S) with a filled epoxy cement. The end-bonding means that the boundary conditions for the classical case of twisting an elastic cylinder are closely approximated. The lower grip (LG) is cemented to the specimen in an identical manner and is also attached to the torque measuring cell (TC).

The design of the cell is based on the conventional strain gauge torque cell.[5] The traditional design calls for four strain gauges arranged as a Wheatstone bridge and mounted on the surface of a cylindrical rod or hollow tube at angles of 45° to the axis of rotation. This configuration is insensitive to all forces and moments except a moment about the central axis of the cell. Furthermore, its response is nearly insensitive to changes in temperature and pressure. Unfortunately, this design could not be made sensitive enough for our application and it is impossible to use a complete bridge inside of the bomb because only three leads are available. (The fourth, or "common" lead described above is not suitable for this purpose because its resistance changes slightly every time the bomb is opened.) Therefore, it was decided to employ a half bridge consisting of two semiconductor strain gauges (SG) mounted at the appropriate angles of a 6 mm (O.D.) aluminum tube. The inner diameter of the tube was 5 mm at the ends but only 0.08 mm near the gauges. To increase the sensitivity of the cell and also to allow pressure relief to its interior, two 3 mm holes were drilled on opposite sides of the cell midway between the gauges. The response of the cell remains linear, but it is now necessary to calibrate for the effects of temperature and pressure. Further, the cell is sensitive to forces and moments that one does not wish to measure, but this is actually an advantage. Under normal circumstances, the deformation of the specimen is closely controlled and it is not expected that any forces other than the torque on the specimen will be seen. If output is observed from the cell before an experiment is started, then it is an indication that something is amiss inside the bomb. This provides the only indication of such problems since the interior of the chamber is cannot be viewed at any time during an experiment.

The other important feature of the lower frame is the slider mechanism (SL) which allows the torque cell to move vertically as the length of the specimen changes. This is particularly important at high pressures because no adjustments can be made under these conditions. Two tiny steel hemispheres attached to the bottom of the torque cell serve to locate the cell approximately in position during installation, but this is only a loose fitting. The cell is prevented from twisting by two teflon balls of 1 mm diameter which roll in grooves on opposite sides of the cell. The balls are placed in holes in the lower frame and are prevented from escaping their positions by set screws on the outside of the lower frame and by a lack of clearance between the frame and the cell. The force of the balls against the grooves is determined by turning the set screws against polyurethane foam springs which lie between the screws and the balls. The screws can be adjusted to minimize the force on the balls while still keeping them secured in the groove. A final constraint is provided by the guide rod (GR) which is also attached to the load cell. The rod slides through a hole in the bottom of the lower frame. This prevents rotation about the axis of the teflon balls - the only remaining degree of freedom other than vertical motion. The vibration of the bath stirring mechanism provides sufficient disturbance to overcome the friction between the balls and the grooves. As a result of these provisions the tensile force on the specimen is no greater than the weight of the lower grip, torque cell, and guide rod, diminished by buoyancy.

The angle through which the specimen rotates is determined by a ratchet (R) and pawl (P) mechanism on the upper frame. The pawl is driven by the motor through gears (G) which multiply the angle of rotation by a factor of 5. Any of five angles between 2° and 15° may be selected. The deformation may be reversed easily by lifting the pawl clear of the ratchet and reversing the motor. A permanent magnet (PM) mounted on the pawl is used to lift it. A repulsive magnetic field is applied to this magnet by an electromagnet wound around the outside of the bomb. The motor itself also contributes to this field. When the specimen is returned to its initial position it runs up against a stop (ST) which establishes the zero strain position.

The angles of rotation at the five stops were precisely determined by placing a mirror on the upper grip and noting the deflection at each position of a beam of light reflected from the mirror. The torque cell was then calibrated by inserting beryllium copper strips of known modulus in lieu of the sample. The device is estimated to have a relative error of 3%.

In contrast to the earlier tensile relaxometer, the maximum operating pressure of the torsional device, although not known, apparently exceeds the safe limit of the bomb (650 MPa) even at -10°C and proved adequate for our goal. Triggering was successful over 80% of the time even at these high pressures. There are only five angles of twist available but this is not a serious limitation. The bomb had to be opened only to change these angles and to install specimens of different diameter. Thus, because of the reset mechanism, several experiments could be conducted in succession without opening the chamber. In practice a mastercurve could be constructed from 14 runs by opening the bomb only twice after the initial insertion. The least satisfactory part of the prototype relaxometer is the method of constraining the slider mechanism. This could be improved in a later version, perhaps by using three or four teflon balls instead of two. Altogether, the torsional relaxometer constitutes a great advance over the original tensile device.

MATERIALS

Stress relaxation, compressibility, and expansivity measurements were made on crosslinked samples of a 1500 type styrene-butadiene copolymer (SBR) and a polybutadiene (BR) having a composition of 55% 1,2-butadiene and 45% 1,4-butadiene.

The styrene-butadiene copolymer was taken from a batch supplied some years ago by the Shell Chemical Company. It was molded into rods having diameters of 12.7 mm and 3.2 mm. The samples were crosslinked with 1 phr of dicumyl peroxide. "Octamine" (Naugatuck Chemicals) was added at 1 phr as an antioxidant. Samples were cured at 155°C for 45 minutes. One specimen of each diameter was used in the relaxation experiments. A short (20 mm) length of the large diameter rod was used in the other experiments.

The polybutadiene was obtained by courtesy of the Firestone Tire and Rubber Company and was labeled "BP 1949" by them. This material was cured for 30 minutes at 160°C with 0.5 phr of dicumyl peroxide in the presence of 1.0

phr of antioxidant. Rods having diameters of 9.5 mm and 3.2 mm were used in the relaxation measurements. A 20 mm rod of 12.7 mm diameter was used for the other experiments.

For stress relaxation in torsion, the rods were cut to about 67 mm in length and cemented to the grips with a filled epoxy cement. It was found that cyanaoacrylate adhesives and unfilled epoxies did not produce good bonds for the high pressure tests.

RESULTS

The shear moduli were referred to the values they would have at the reference temperature T_o and the reference pressure P_o. The theory of reduced variables[4] suggests that the modulus in the reference state, $G_p(t)$, can be obtained from $G(t)$ by the correction $G_p(t) = pG(t)$, where $p = \rho_o T_o / \rho T$. This correction requires the density, which was obtained from the Murnaghan equation, eq. (6), below. The temperature correction was also made everywhere although, strictly speaking, it should not be applied outside of the rubbery region. In any case its largest value was only 0.12 logarithmic units. The reduced isothermal moduli, $G_p(t)$, are plotted as functions of time in logarithmic coordinates in Figures 2-5 for SBR and in Figures 6-9 for BR. Figures 3 and 7 show data obtained under a range of pressures at 5°C. Figures 2, 4, and 5 (SBR) and 6, 8, and 9 (BR) show segments obtained at constant pressures of 0.1, 200 and 340 MPa, respectively. Some of the data segments were shifted downwards by the offset A shown next to the curve. The A's were introduced for clarity and are zero when no explicit value is given.

Mastercurves were constructed in the usual way by shifting the reduced data segments into superposition along the log t axis. Figures 10 and 11 and Figures 12 and 13 show the mastercurves for SBR and BR, respectively. In Figures 10 and 12, curves (A) and (D) represent the isobaric behavior at 0.1 MPa isothermal behavior of the material at 5°C, respectively. In Figures 11 and 13 curve (A) is repeated in order to allow comparison with curves (B) and (C) which result from the isobaric experiments at 200 and 340 MPa, respectively. The superposition of curves (A) and (D) over the transition zone and the rubbery region indicates that the materials are thermo- and piezorheologically simple. It is expected that there will be no superposition in the glassy region since the high pressure glasses undergo densification as they approach vitrification and we expect the denser materials to have a higher modulus. This had also been observed earlier.[1,2] Curves (A), (B), and (C) can also be brought into superposition by appropriate shifts along the log-time axis. The symbols in the insets in Figures 10 and 12 show the shift distances used to create the isobaric mastercurve (A). The shifts employed to construct curves (B), (C), and (D) are shown by the symbols in Figures 15 and 14 for SBR and in Figures 17 and 16 for BR. The significance of the solid and dashed lines in these figures will be explained later.

The FMT theory requires that the coefficient of thermal expansion and the bulk modulus and its pressure dependence be known for the material in the rubbery state. These quantities were determined from measurements in the extensometer. Figure 18 shows the volume (converted from length measurements) as a function of temperature obtained at a constant cooling rate of 30°C per hour for both materials. The intersection of the rubbery and glassy slopes yields the glass transition temperatures, T_g, of -61.2°C for SBR and -55.0°C for BR. We know of no data with which to compare the T_g of our BR sample. The T_g determined for SBR is at the low end of the reported range.[4,7] Figure 19 shows the typical volumetric behavior of both materials under hydrostatic pressure. The slopes of the volume-temperature curves at zero pressure are inversely related to K_T^*, the bulk modulus at zero pressure. These values are shown for the rubbery region in Figure 20. The temperature dependence of K_T^* is well described by the Gee equation[8]

$$K_T^*(T) = K_{T\mathrm{o}}^*(T)\exp - \beta_T^*(T - T_\mathrm{o}). \tag{4}$$

If we define the compressibility, κ, through the equation

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{5}$$

where V is the volume (or specific volume if desired), then the integration of eq. (4) yields the Murnaghan equation[9]

$$V = V_0\left[\frac{K^*(T) + kP}{K^*(T) + kP_\mathrm{o}}\right]^{-1/k}. \tag{6}$$

A non-linear fit of this equation to each set of isothermal volume-temperature data yields different values of k_T at each temperature. As described previously,[3] we averaged these values, which do not appear to be correlated with temperature, to obtain a single value of k_T. This value is then used to redetermine the non-linear fit to eq. (6) with $K_T^*(T)$ as the only undetermined coefficient at each temperature. This procedure results in a better agreement with Gee's equation than does the use of the individual k_T's determined at each temperature. Both values of the averaged k_T are slightly above the "universal" value[3] of 10.2. We were unable to obtain any of these parameters in the glassy region because the temperatures were too low to be reached by our equipment. In any event, we have already shown[3] that such information is only marginally useful. Values of the experimentally derived quantities are shown in Table I.

DISCUSSION

There are several points worth noting about the superposition of the relaxation data. The vertical shifts (i.e., shifts in log $G_p(t)$) which were required in the earlier work of Fillers and Tschoegl[1] in tension on Hypalon 40 and Viton B,

Table I

Experimental Parameters

Parameter†	SBR	BR
V_o [cm^{3}g^{-1}]	1.035	1.070
α_r^* [10^{-4}K^{-1}]	6.69	7.46
α_g^* [10^{-4}K^{-1}]	3.07	3.62
$\Delta\alpha$ [10^{-4}K^{-1}]	3.62	3.84
T_g [°C]	-61.2	-55.0
K_r^* [MPa]	2100	2050
$K_r^*(T_g + 47°C)$ [MPa]	2310	2170
k_r	10.8	11.4
β_r^* [10^{-3}K^{-1}]	4.81	4.27

† The reference temperature, T_0, is 5° for both materials

were not necessary for either SBR or BR in shear. Certain data segments could have been brought into slightly better superposition with vertical shifts, but such shifts were not made. Those shifts which one might choose to apply would be much smaller than those needed previously.[1] As mentioned previously, Fillers and Tschoegl made their measurements in tension but reported their results as $G(t)$. The vertical shifts associated with the data did not result from this conversion - they were needed whether the data were presented as $E(t)$ or as $G(t)$. However, because the conversion was approximate, it is impossible to decide whether these shifts resulted from an experimental artifact or from the effect of pressure on $E(t)$. If they were an artifact, they were probably due to the method of correcting for the change in length of the specimen. The slider mechanism of the torsional relaxometer insures that this problem did not occur in the experiments reported here.

According to the theory of elasticity, the following relation holds between G and E:

$$E = \frac{9KG}{3K + G}. \tag{7}$$

For time-dependent materials the s-multiplied Laplace transforms must be substituted for these quantities. Transformation back to the time domain yields three convolution integrals which cannot be solved explicitly for either $E(t)$ or $G(t)$. Since the shear modulus, G, represents material response to an isochoric deformation, it is expected to be independent of pressure. Our experiments confirm this since all the pressure dependence of $G(t)$ can be described by the two shift factors, $a_{T,P}$ and p, which account for its time and temperature dependence. However, the pressure dependence of the bulk modulus, $K = -P\, V_0/\Delta V$, implies that $E(t)$ is also a pressure dependent quantity. It is uncertain, then, whether $E(t)$ and $G(t)$ yield the same information on the effect of pressure on stress relaxation. A test would require use of both the torsional and the tensile relaxometer. Unfortunately, the tensile relaxometer does not function under the conditions necessary to perform such tests.

The mastercurves shown in Figures 10 - 13 show slightly more scatter than was found in the tensile experiments. One reason for this is that we chose not to apply any vertical shifts to log $G_p(t)$. Also, temperature control was slightly better in the tensile tests. In the shear tests the refrigeration equipment was forced to the limits of its capabilities, since SBR and BR required lower temperatures than Hypalon 40 and Viton B. There is also evident in most of the mastercurves a very slight thickening of the curve at the rubbery end of the transition zone. This was also observed in the tensile experiments and may simply be due to the fact that the density of points in this area is higher than in the surrounding zones.

We can now proceed to test the applicability of the FMT equation. This equation reduces to the WLF equation[4] at constant pressure. The inserts in Figures 10 and 12 show the predictions of a linearized fit of the shift distances to the WLF equation as the solid curves. Following the procedure introduced previously,[3] the value of c_1^{oo} obtained from this fit is used together with the bulk modulus, K_T^*, and the Bridgman constant, k_T, to fit the isothermal shift data. The fit, shown as the solid lines in Figures 14 and 16 for SBR and BR, respectively, is very good. Values of f_0, K_φ^*, and k_φ are derived directly from this fit, with B and α_f^* being obtained from c_1^{oo} and c_2^{oo}. A summary of these data is shown in Table II.

Table II

Material Parameters

Parameter†	SBR	BR
c_1^o	5.61	5.12
c_2^o [°C]	92.5	105.2
B	0.699	0.818
f_o	0.0541	0.0694
f_g	0.0156	0.0298
α_f^* [$10^{-4}K^{-1}$]	5.84	6.60
α_φ^* [$10^{-4}K^{-1}$]	0.81	0.85
K_φ^* [MPa]	2840	3320
$K_\varphi^*(T_g + 47°C)$ [MPa]	3130	3510
k_φ	17.4	18.2

† The reference temperature, T_0, is 5° for both materials

Both values of k_φ are substantially higher than k_T as observed before,[2] but they both lie between the values of 15.8 and 36.0 found earlier for Hypalon 40 and Viton B. The quantities B, which have often been thought to be near unity, have again been found to be significantly less than 1, although a little less so than before. The assumption that $B = 1$ is certainly untenable. The coefficient of expansion of the occupied volume, α_φ^*, is quite small, in agreement with the notion that the occupied volume is fairly rigid. We have also included in Tables I and II information on the bulk moduli at $T_g + 47$°C. This is for comparison with the earlier tensile experiments in which T_0 was equal to $T_g + 47$°C for both materials. The ratio of K_φ^* to K_T^* at this condition is roughly 1.5 for all four materials.

The FMT equation can be used to predict thermorheological shifts at constant high pressures.[2] The predictions are shown as the solid lines in Figures 15 and 17 for SBR and BR, respectively. A further assumption is necessary in order to make these predictions. This has been discussed in detail elsewhere.[2] The assumption concerns the expansivity of the free volume at high pressures which has not been needed up to this point. According to the FMT theory, at a new reference pressure, P_0', α_f is given by

$$\alpha_f(P_0') = \alpha_f^* - \left(\frac{\beta_T^* P_0'}{K_T^* + k_T P_0'} - \frac{\beta_\varphi^* P_0'}{K_\varphi^* + k_\varphi P_0'}\right) \qquad (8)$$

where β_φ^*, the occupied volume analog of β_T^*, is unknown. A suitable value for it must be assumed. Earlier[2], we showed that for Hypalon 40 and Viton B $\beta_\varphi^* = \beta_T^*$ seemed to be the best of several assumptions. This is again the case with SBR and BR. The comparison with other assumptions is not shown. Knowing $\alpha_f(P)$ allows us to calculate the fractional free volume, $f\,(T_0,P_0)$, at the new reference conditions.[2] This, in turn, permits us to calculate the WLF constants at the new reference pressure, P_0'. The predictions of this method appear as the solid lines in Figures 15 and 17. The agreement is excellent at both higher pressures.

Several other proposals have been made for describing time-pressure superposition. O'Reilly[10] found that dielectric measurements were represented by the simple relation

$$\log a_{T_0,P} = C(P - P_0) \tag{9}$$

where C is a constant characteristic of the material. Recently Fytas, et al.,[11,12] have shown that O'Reilly's result can be obtained by extending the viscosity theory of Sanchez[13] to high pressures. They have also studied several materials at high pressures by photon correlation spectroscopy and have found agreement with O'Reilly's equation. The data presented here are certainly in disagreement with eq. (9). This is somewhat surprising since it is well known that shifts from isobaric dielectric measurements can be described by the WLF equation, often with parameters very close to those found from mechanical spectroscopy. The reason for this disagreement is not clear.

The theory of Adam and Gibbs[14] describes the glass transition in terms of the configurational entropy of the system. The predictions of the theory are extremely close to those given by the WLF equation. Havlícek, Ilavský, and Hrouz[15] (HIH) have extended the Adam-Gibbs theory to high pressures. Their equation for the shift factor takes the form

$$\log a_{T,P} = [h(T,P) - h(T_0,P_0)]/2.303 \tag{10}$$

where

$$h(T,P) = m/T[\Delta C_p \ln(T/T_2^0) - V_0(\Delta\alpha P - aP^2/2)]\,. \tag{11}$$

Here m is a constant characteristic of the material, ΔC_p is the change in heat capacity associated with vitrification at the reference pressure, P_0, T_2^0 is the temperature below which the number of configurations decreases to the order of unity[16] at the reference pressure, and a is the pressure derivative of $\Delta\alpha$ at the reference temperature. The authors assume that the thermal expansion coefficient, or at least the difference, $\Delta\alpha$, decreases linearly with pressure. This is at odds with the FMT theory according to which $\Delta\alpha$ should follow an analog of eq. (8) in which glassy quantities replace those of the occupied volume. (In Appendix D, an alternate form of the HIH equation is developed using such an analog.) In fact, Figure 1a of the HIH paper suggests that their assumption is not followed at high pressures. Nevertheless, the theory is very appealing, since there are no undetermined parameters and all parameters except a can be measured at atmospheric pressure.

The parameters necessary to test the predictions of this theory on our materials have been obtained. The ratio of m to ΔC_p and the temperature T_2^o can be found from a non-linear least squares fit of the isobaric shift data to the Adam-Gibbs equation, which is the form taken by eqs. (10) and (11) when $P = P_0 = 0$. The value of ΔC_p for SBR was taken from the work of Furukawa, McCoskey, and Reilly.[17] For BR, the value was estimated from the "bead" theory[18], which also gave a good estimate for SBR. The materials studied previously, Hypalon 40 and Viton B, are included in this comparison. Values of ΔC_p for these materials were measured in a DTA apparatus.[19] Although values for a are available for Hypalon and Viton, it was decided to allow a to be determined by a fit to the data at constant temperature. Table III provides a summary of the data for the HIH equation.

The predictions of the HIH theory are shown in Figures 14, 16, and 21 as the dotted-dashed lines. The agreement is not very good. The slope at zero pressure $(\partial \log a_{T_0,P}/\partial P)_{P=0}$ is responsible for much of the error. Under these circumstances it is pointless to attempt predictions at higher fixed pressures since a reference condition cannot be established.

The HIH reduces to simple forms in the special cases of constant temperature and pressure. In the isobaric case, the Adam-Gibbs equation is

Table III

Parameters for the HIH Equation

Parameter	SBR	BR	Hypalon 40	Viton B
T_o [°C]	5.0	5.0	25.0	25.0
T_2^o [°C]	-88.64	-101.7	-35.2	-34.3
$m/\Delta C_p$ [10^{3}°K^{-1}]	1.280	1.350	0.376	0.307
ΔC_p [10^{3}Jkg^{-1}K^{-1}]	0.520	0.407	0.376	0.188
α [10^{7}KMPa^{-1}]†	2.14	4.84	15.0	20.5

† Parameter determined from a fit to the data.

recovered. We have

$$\log a_{T,P_o} = -\frac{a_1^o(T - T_o)}{a_2^o(T) + T - T_o} \tag{12}$$

where

$$a_1^o = m/2.303 T_o \Delta C_p \ln(T_o/T_2^o) \tag{13}$$

and

$$a_2^o(T) = \frac{T_o \ln(T_o/T_2^o)}{\ln(T_o/T_2^o) + [1 + T_o/(T - T_o)]\ln(T/T_o)} . \tag{14}$$

With good approximation,

$$(1 + T_o/(T - T_o)) \ln(T/T_o) \approx 1 , \tag{15}$$

and then the slight temperature dependence of a_2^o disappears and the Adam-Gibbs equation becomes identical with the WLF equation. At constant temperature T_o we find

$$\log a_{T_o,P} = \frac{a_1^o \gamma(P)}{a_2' - \gamma(P)} \tag{16}$$

where

$$a_2' = \ln(T_o/T_2^o) \tag{17}$$

is a constant and

$$\gamma(P) = mV\Delta\alpha / 2.303\Delta C_p V(\Delta\alpha P - aP^2/2)\ln(T_o/T_2^o)\,. \tag{18}$$

The FMT theory gives, again at constant temperature,

$$\log a_{T_o,P} = \frac{c_1^o \zeta(P)}{c_2' - \zeta(P)} \tag{19}$$

where

$$c_2' = c_2^o k_r \alpha_f = k_r f_o \tag{20}$$

and

$$\zeta(P) = \ln\left[\frac{1 + c_4^o P}{1 + c_4^o P_o}\right] - \frac{k_r}{k_\varphi}\ln\left[\frac{1 + c_6^o P}{1 + c_6^o P_o}\right]. \tag{21}$$

Thus the HIH and FMT equations are formally equivalent under restricted conditions. By eq. (16) the initial slope of log $a_{T_o,P}$ vs. P is proportional to $m\Delta\alpha/(cp)^2$. Taking the Adam-Gibbs parameters $m/\Delta C_p$ and T_2^o as fixed by the isobaric fitting leaves $\Delta\alpha$ and ΔC_p as "adjustable parameters." Repeating the fit to the isothermal shift data with these new variables yields a much better agreement (not shown in the figures). However, the values of the parameters, particularly ΔC_p, change significantly. In the case of Hypalon 40, ΔC_p must be doubled. Although the Adam-Gibbs and HIH theories make simplifying assumptions about the pressure and temperature dependence of ΔC_p one would expect at least that the initial slope of the log $a_{T_o,P}$ curve would be correctly predicted even if ΔC_p varied somewhat with temperature and pressure. This is not the case. Similarly, $\Delta\alpha$ also changes but relatively less than ΔC_p.

ΔC_p is the difference between the heat capacities of the rubber and the glass. We had shown[8] that the difference, $\Delta\alpha$, between the expansivities of the rubber and the glass, apparently in analogous fashion, does not lead to successful predictions from the free volume theory, either. The latter, however, in fact requires the expansivity of the occupied volume rather than that of the glass. Analogy suggests that the heat capacity of the glass be replaced by another parameter. Unfortunately, the Adam-Gibbs theory does not admit such an analogy. If $\Delta\alpha$ and ΔC_p are obtained from an isothermal fit according to eq. (16), the slope is correctly predicted. However, the agreement at high pressures is still less satisfactory than with the FMT theory because the assumed pressure dependence of $\Delta\alpha$ lacks the correct form.

Some work has been reported recently on applying the Simha-Somcynsky (SS) equation of state[20] to viscoelastic response at high pressures. The SS equation is a hole theory of the liquid state which is known to have applicability to many classes of materials, including small molecules, homogeneous liquid mixtures, and polymers. There are two simultaneous equations to be obeyed:

$$\tilde{P}\tilde{V}/\tilde{T} = [1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \quad (22)$$

and

$$\begin{aligned} y^{-1}\ln(1-y) = {} & (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \\ & + [2^{-1/6}y(y\tilde{V})^{-1/3} - 1/3][1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} . \end{aligned} \quad (23)$$

Equations (22) and (23) are valid only for long chain molecules. Here, $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, and $\tilde{P} = P/P^*$ are reduced variables defined in terms of the characteristic volume, temperature, and pressure, V^*, T^*, and P^*, respectively.† The quantity y is the fraction of occupied lattice sites. It is tempting to try to relate the quantity y to the occupied volume. Curro, Lagasse, and Simha[21] proposed $1 - y$ as a representation for the free volume fraction, f.

With this assumption it is possible to compute the shift factor from the Doolittle equation[4] provided the characteristic quantities V^*, T^*, and P^* are known. The first two of these can readily be determined from expansivity

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† The notation for the characteristic parameters does not follow the conventions outlined in the introduction. The asterisks have no relation to zero pressure.

measurements while P^*, which is not needed if the investigation is confined to atmospheric conditions, can be found from compressibility measurements.[22] The SS parameters for the materials studied here are shown in Table IV.

Table IV

Parameters for the SS Theory

Parameter	SBR	BR	Hypalon 40	Viton B
V^* [cm^{3}g^{-1}]	1.0267	1.0520	0.8137	0.4964
T^* [K^{-1}]	9360.	8770.	8740.	9010.
P^* [MPa]	877.	912.	1150.	1070.
P_s^* [MPa]	1600.	1500.	2570.	1380.
α_y [10^{-4}K^{-1}]	5.96	6.48	6.61	6.37
α_y/α_f	1.019	0.983	1.037	1.079
$f_{y\circ}$	0.0552	0.0681	0.0402	0.0371
B_y	0.712	0.804	0.277	0.206
$y_\circ$	0.9364	0.9250	0.9112	0.9172
δ	0.0084	0.0069	0.0486	0.0457

With the assumption $f = 1 - y$, Simha, Curro, and Lagasse were able to describe aging data on poly(methyl methacrylate). However, there are two problems with their results: (1) they did not consider all of the available experimental data in the liquid range, and (2) the values of the free volume parameters which they derived from the data are unrealistic. The second problem is minor and can be avoided by merely stating that f is proportional to $1 - y$ rather than equal to it. The first problem is more serious. Only the upper half of the available data[23] for log a_T shows agreement with the assumption.

It is possible to take a closely related, but slightly different approach.[24] The quantity y, as predicted by eqs. (22) and (23), is linear with temperature over a wide range of temperature at any reasonable pressure. Thus we can let f be linearly related to y and still obtain a WLF type of relationship for the isobaric shift factor predicted from the Doolittle equation. If we let $f_y = -c(y + b)$ then the estimate for α_f is automatically a constant. A comparison of

$$\alpha_y = -(\partial y/\partial T)_P|_{P=P_0, T=T_0} \, . \tag{24}$$

(Table IV) with α_f (Table II) suggests that c is close to unity. We then choose $b = 1 - \delta$ for convenience so that

$$f_y(T,P) = 1 - y(T,P) - \delta \, . \tag{25}$$

Equation (25) follows from a suggestion of Utracki[24,25] who has successfully applied the idea to viscosity-pressure studies of a homologous series of small molecules as well as polymers. The concept is easily extended to the shift factor. We have

$$\log a_{T,P} = \frac{B_y}{2.303}\left[\frac{1}{1 - y - \delta} - \frac{1}{1 - y_0 - \delta}\right] \tag{26}$$

where y_0 is the fraction of unoccupied sites at the reference conditions, determined from eqs. (22) and (23), and

$$B_y = 2.303 c_1^0 c_2^0 \alpha_y \, . \tag{27}$$

In practice the quantity δ, representing the fraction of vacant SS lattice sites not available as free volume, is found from

$$\delta = 1 - y_0 - f_{y0} \tag{28}$$

where

$$f_{y0} = c_2^0 \alpha_y \tag{29}$$

is the estimate of the free volume at the reference conditions. Table IV lists the values obtained for δ and the free volume parameters determined from eqs.

(24), (27), (28), and (29). Contrary to the assumptions of the free volume theory, B_y, α_y, and δ depend somewhat on the choice of reference temperature. The parameters B, α_y, and f_{y0} differ only slightly from B, α_f, and f_0 as illustrated by the ratio α_y/α_f in Table IV. The sign of δ, which is opposite to that found by Utracki, suggests that the SS theory overestimates the fraction of lattice sites which are available as free volume. In this interpretation, some empty sites would be true holes (free volume) while others would be considered unavailable for motion. The problem of unavailable sites has recently been discussed by Brostow.[26]

Unfortunately, at high pressures f_y is still not a good estimate of f. There are two simple alternatives for correcting this. One is to let δ depend on pressure. This assumption does not render a realistic value for α_f at higher pressures. The second alternative, again suggested by Utracki,[25] is to take note of the fact that the SS equation is a thermodynamic relationship, whereas the phenomenon of interest (shear) is mechanical in nature. Hence it is perhaps unreasonable to expect eqs. (22) and (23) to describe the behavior adequately, at least with characteristic values not associated with shear. We can determine a characteristic pressure in shear, P_s^*, by shifting a plot of log (log $a_{T,P}$) vs. log P over a theoretical plot with an ordinate of log $\tilde{P}$. Utracki, studying viscosity at high pressure, found that only a few of the materials he studied required a P_s^* differing from P^*. All four of the materials studied by us yielded P_s^* values which were substantially larger than P^*. This may be taken to indicate that the free volume does not decrease nearly as rapidly as does the fraction of empty lattice sites. The determination of the free volume parameters and P_s^* from the SS theory does not exactly follow the method of Utracki, who considered only liquid viscosities, and determined the parameters δ and P_s^* without the use of the WLF constants.

The isothermal predictions of the SS theory using P_s^* and eq. (26) are shown in Figures 14, 16, and 21 as the dashed lines. The agreement is good, at least good enough to allow further prediction of the shift factor at higher fixed pressures. Those predictions are shown in Figures 15, 17, 22, and 23. Generally, the predictions diverge from the data at temperatures far from the reference condition, except in the case of Viton B (Figure 23) for which, at 100 MPa, the agreement here is better than that with the FMT equation. This, however, is probably fortuitous. The method just outlined contains a single adjustable parameter, P_s^*. Nevertheless, it yields predictions which are better than those of the HIH equation, even when this is used with three adjustable parameters. It is also superior to the use of glassy parameters as substitutes for those of the occupied volume.[3]

One of the goals of this project has been the determination of the values of the free volume parameters for different materials. For the materials examined so far, the parameters f_g and α_f have been in the range generally expected although significantly different from values estimated from isobaric shifts alone, since the parameter B turns out to be substantially different from 1. The parameters α_f, B, and f_g can be estimated from eqs. (24), (27), and (29) if V^*, T^*, and the WLF parameters are available. It is convenient to select $T_g + 50°C$ as the reference temperature so that the parameters characterizing different materials can be more clearly compared. Table V shows the calculated quantities for a number of polymers. In constructing the table it was found, not surprisingly, that the thermodynamic parameters showed much more precision than the viscoelastic ones. Hence only one arbitrarily selected set of SS parameters is shown, even when several are available. The choice is not critical. The table reveals a rather broad variation in the value of B. Of some interest are the results for the estimated expansivity of the free volume, α_v and the free volume fraction, f_{vg}, calculated from α_v and c_1^g. In all cases but one (to be discussed below) the expansivity is not strongly temperature dependent. All materials show f_{vg} in the range 0.02 - 0.07. This is somewhat larger than expected. The highest f_{vg}'s are associated with negative values of δ, indicating that the free volume exceeds the number of empty SS lattice sites. Utracki's results suggest that this problem does not affect the predictive power of the method. It is also noteworthy that in all cases but one the estimated α_f exceeds $\Delta\alpha$. This is not true of the traditionally quoted value α_f / B when compared to $\Delta\alpha$.

The case of poly(dimethyl siloxane) (PDMS) is an exception. An examination reveals that the reduced glass transition temperature, $\tilde{T}_g$, is quite small and $(\partial y / \partial T)_{P=0}$ is strongly temperature dependent in the region of T_g. Hence, the method fails to agree with the WLF equation and it is not surprising that the predicted parameters are unreasonable near T_g. However, estimations based on eqs. (24) and (25) may be expected to be successful at room temperature for PDMS. Utracki[25] has, in fact, successfully predicted the high pressure viscosity of this material near room temperature.

CONCLUSION

The free-volume-based FMT equation is able to describe the superposition of stress relaxation data at high pressures. We suspect that the free volume theory is successful because it does not consider the ill-defined glassy state. The parameters derived from the Adam-Gibbs theory at atmospheric pressure do not seem appropriate for the description of relaxation at high pressure. This conclusion remains true regardless of the choice of representation for $\Delta\alpha(P)$. The extension of the Simha-Somcynsky equation of state to this problem yields reasonable predictions for the polymers studied with only a single adjustable parameter, P_s^*. The fact that the theory provides an excellent estimate for the expansivity of the free volume answers one of the objections to the free volume theory, namely, that the free volume is too ill-defined to be operationally useful. Even without the parameter P_s^* the theory predicts realistic values for the fractional free volume, its expansivity, and the proportionality factor B in most cases, provided the parameters of the SS theory and the zero pressure WLF constants are available.

Table V

Free Volume Parameters from the SS Theory

	Expt.	T_g[K]	c_1^g	c_2^g [K]	V^* [cm^{3}g^{-1}]	T^* [K]	B_g	f_{vg}	α_g [K^{-1}] ×10^4	$\Delta\alpha$ [K^{-1}] ×10^4	δ	Ref.
Poly(methyl acrylate)	V	275	9.11	110	0.7925	9200	1.47	0.0382	6.36	4.0	0.0260	27,4
	SR	276	8.57	95.0			1.19	0.0286		2.9	0.0355	28,29,30
Poly(vinyl acetate)	V	308	8.61	110	0.8140	9410	1.37	0.0377	6.31	3.9	0.0425	27,30
	SR	305	7.64	96.8			1.07	0.0298	6.30	4.09	0.0508	28,30,31
Polystyrene	V	371	6.47	97.5	0.9626	12700	0.661	0.0216	4.55	3.7	0.0389	32,4
	SR	371	6.26	77.6			0.508	0.0125		3.0	0.0479	30,32
Poly(α-methyl styrene)	VR	445	8.68	103.5	0.9231	12790	0.961	0.0249	4.65	3.6	0.0677	33
atactic Poly(methyl methacrylate)	V	381	9.11	130	0.8433	11910	1.35	0.0396	4.94	3.05	0.0367	27,30
	SR	379	9.11	136			1.41	0.0425	4.93	3.8	0.0337	34,35
Poly(ethyl methacrylate)	V	335	10.4	120	0.8862	11640	1.45	0.0351	5.02	3	0.0242	27,4
	SR	335	9.98	115.5			1.33	0.0329		3.1	0.0265	35,36
Poly(n-butyl methacrylate)	V	300	10.3	130	0.9415	10540	1.69	0.0439	5.49	2.7	0.0122	27,35
	SR	300	11.2	146.6			2.07	0.0530		2.3	0.0031	37,38
Poly(n-hexyl methacriyate)	V	268	10.3	140	0.9727	9980	1.90	0.0518	5.75	2-3	-0.0046	27,4
	SR	268	12.8	179.4			3.05	0.0744			-0.0273	39
Poly(n-octyl methacrylate)	SR	253	11.0	157.3	1.0058	9770	2.32	0.0626	5.83	2-3	-0.0207	40,4
Poly(dimethyl siloxane)	SR	150	3.5	119	0.9690	8160	0.624	0.0445	6.45	9.3	-0.0413	41,30

$T_o = T_g + 50K$
Letters in the Expt. column refer to the type of experiment:
SR: shear relaxation, V: viscosity, VR: volume recovery.

Additional WLF constants from dielectric measurements may be found in Sanchez.[13]
The characteristic parameters were obtained from Simha and Wilson.[48]

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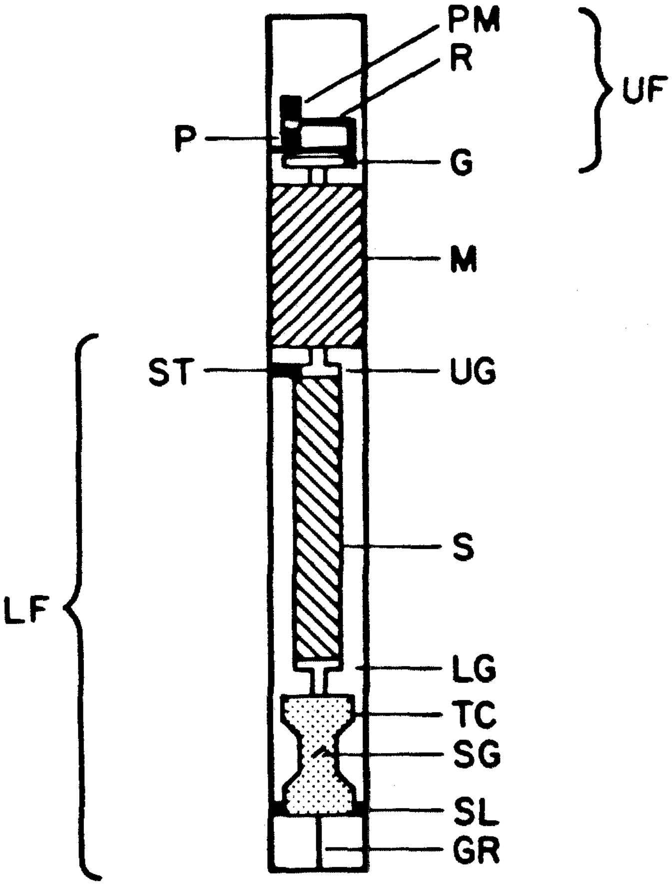

Figure 1. Torsion Relaxometer. Letters are explained in the text.

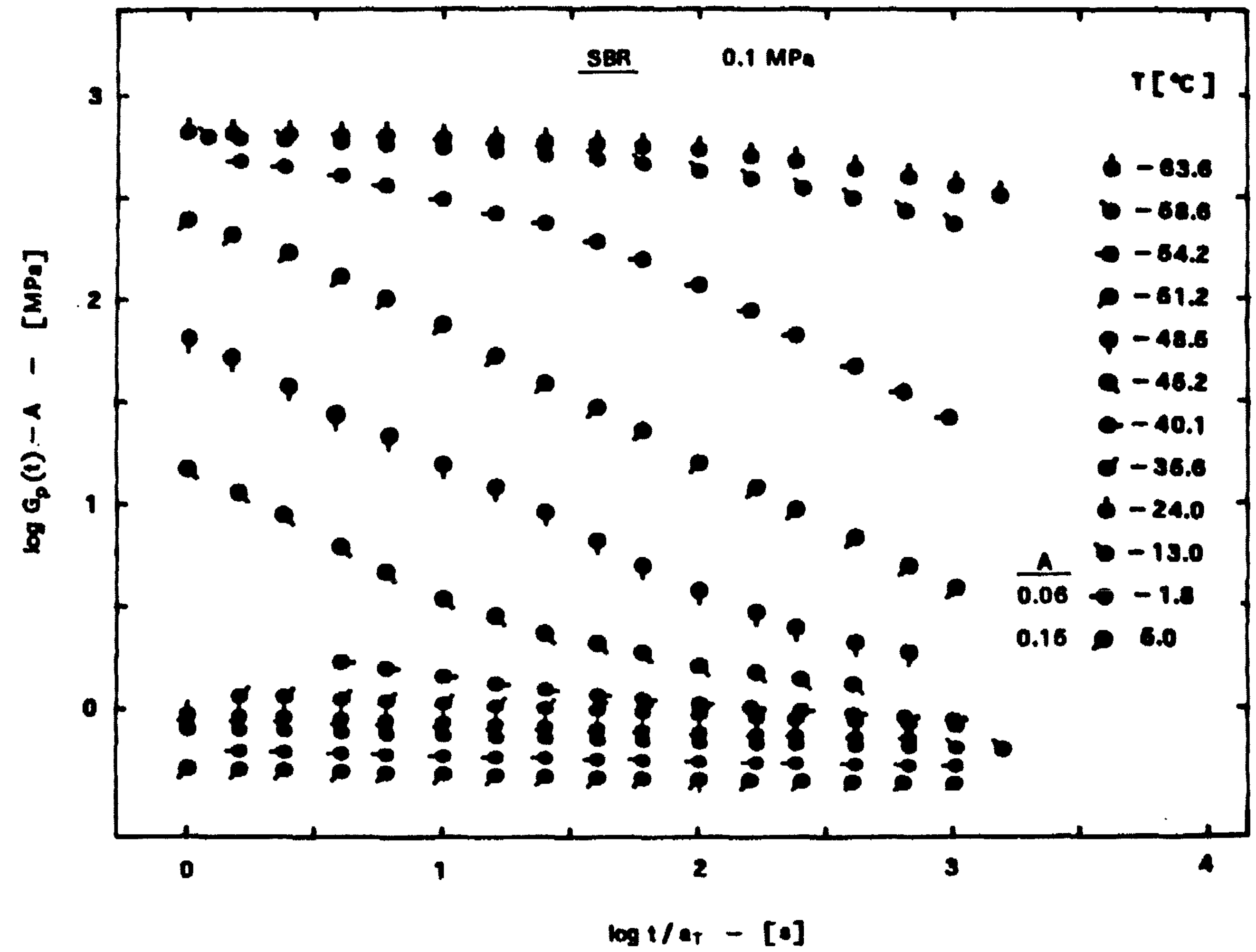

Figure 2. Styrene-butadiene rubber shear modulus $G_p(t)$ at and 0.1 MPa and temperatures indicated.

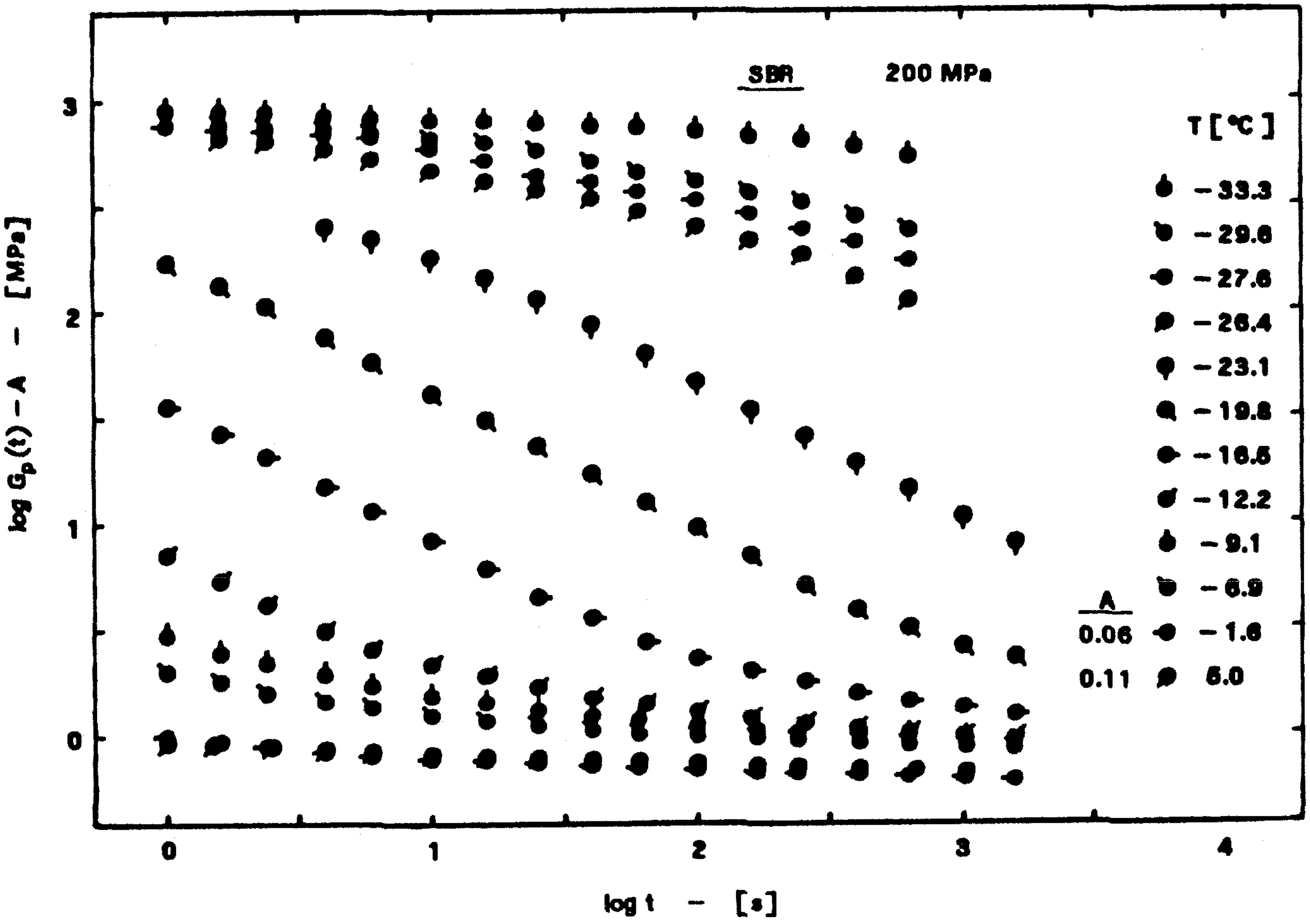

Figure 3. Styrene-butadiene rubber shear modulus $G_p(t)$ at 5^oC and pressures indicated.

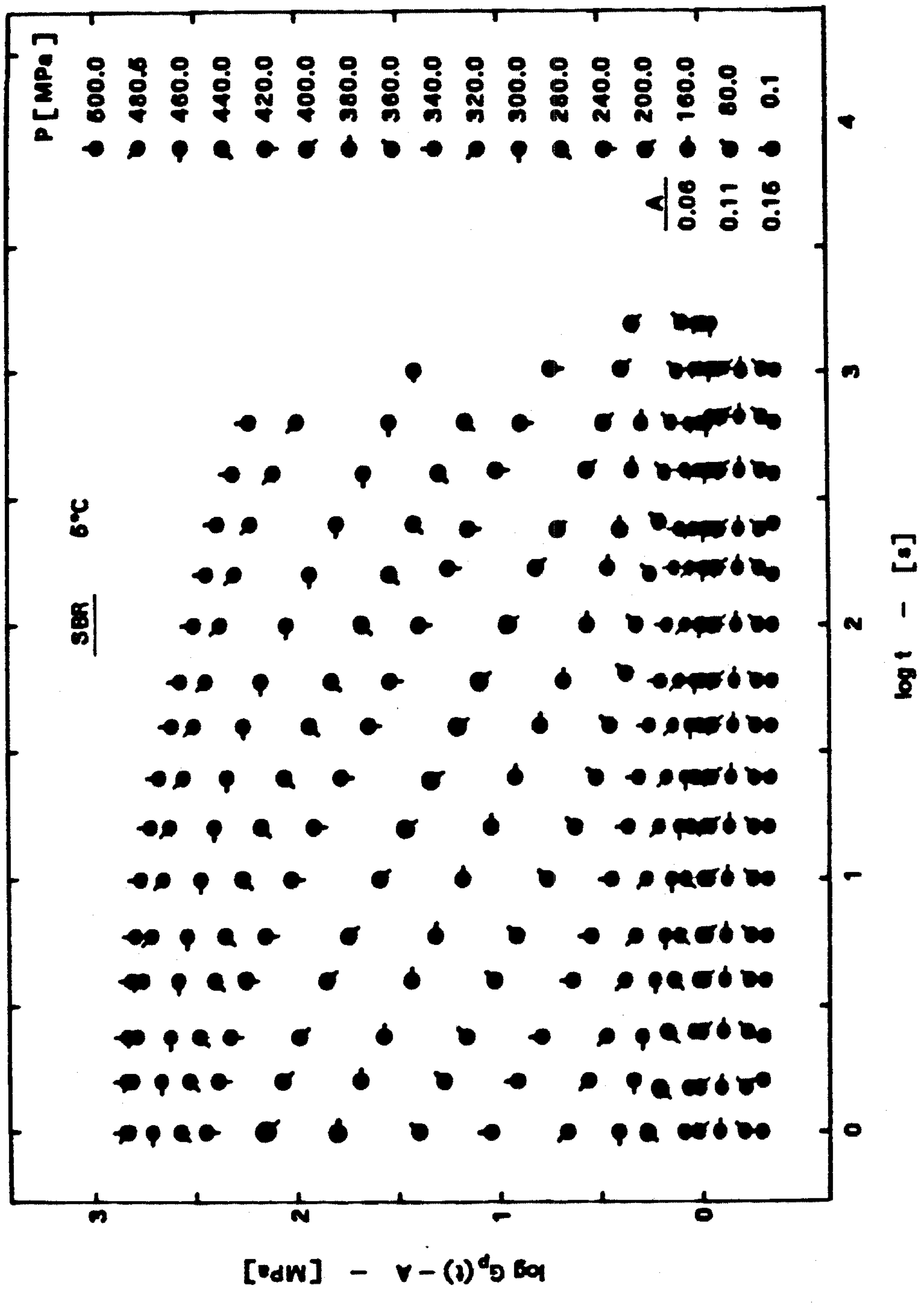

Figure 4. Styrene-butadiene rubber shear modulus $G_p(t)$ at 200 MPa and temperatures indicated.

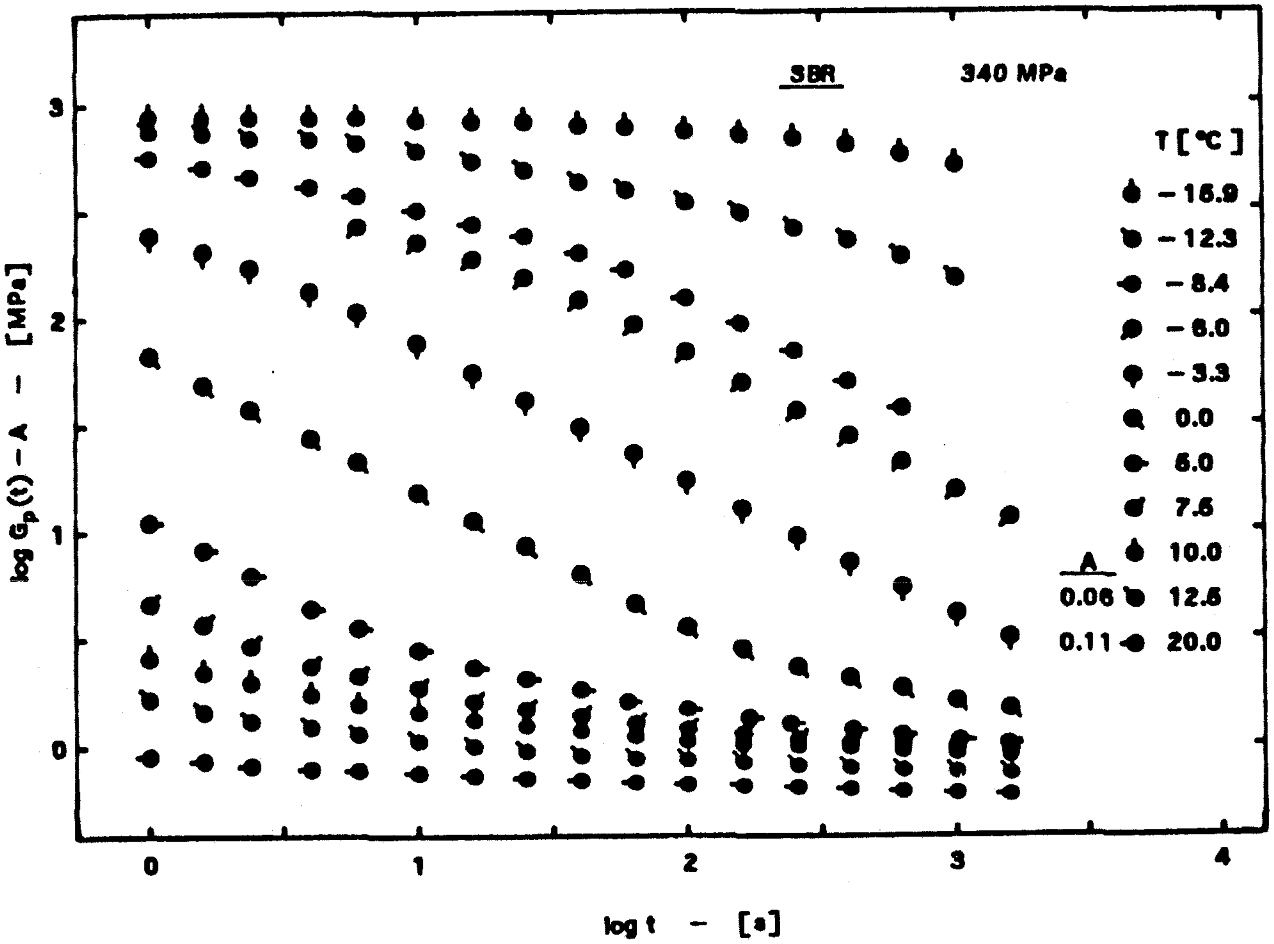

Figure 5. Styrene-butadiene rubber shear modulus $G_p(t)$ at 340 MPa and temperatures indicated.

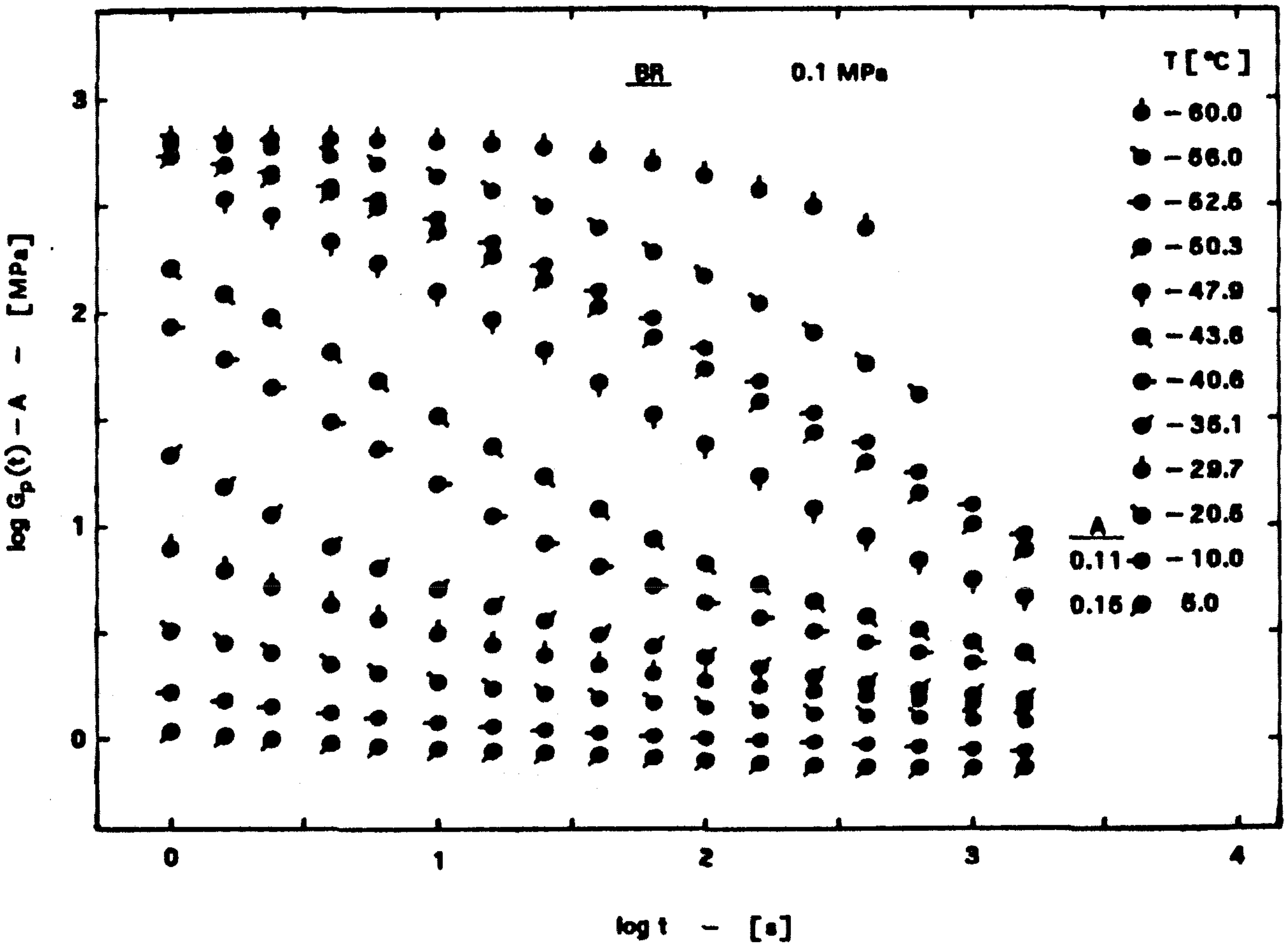

Figure 6. Butadiene rubber shear modulus $G_p(t)$ at 0.1 MPa and temperatures indicated.

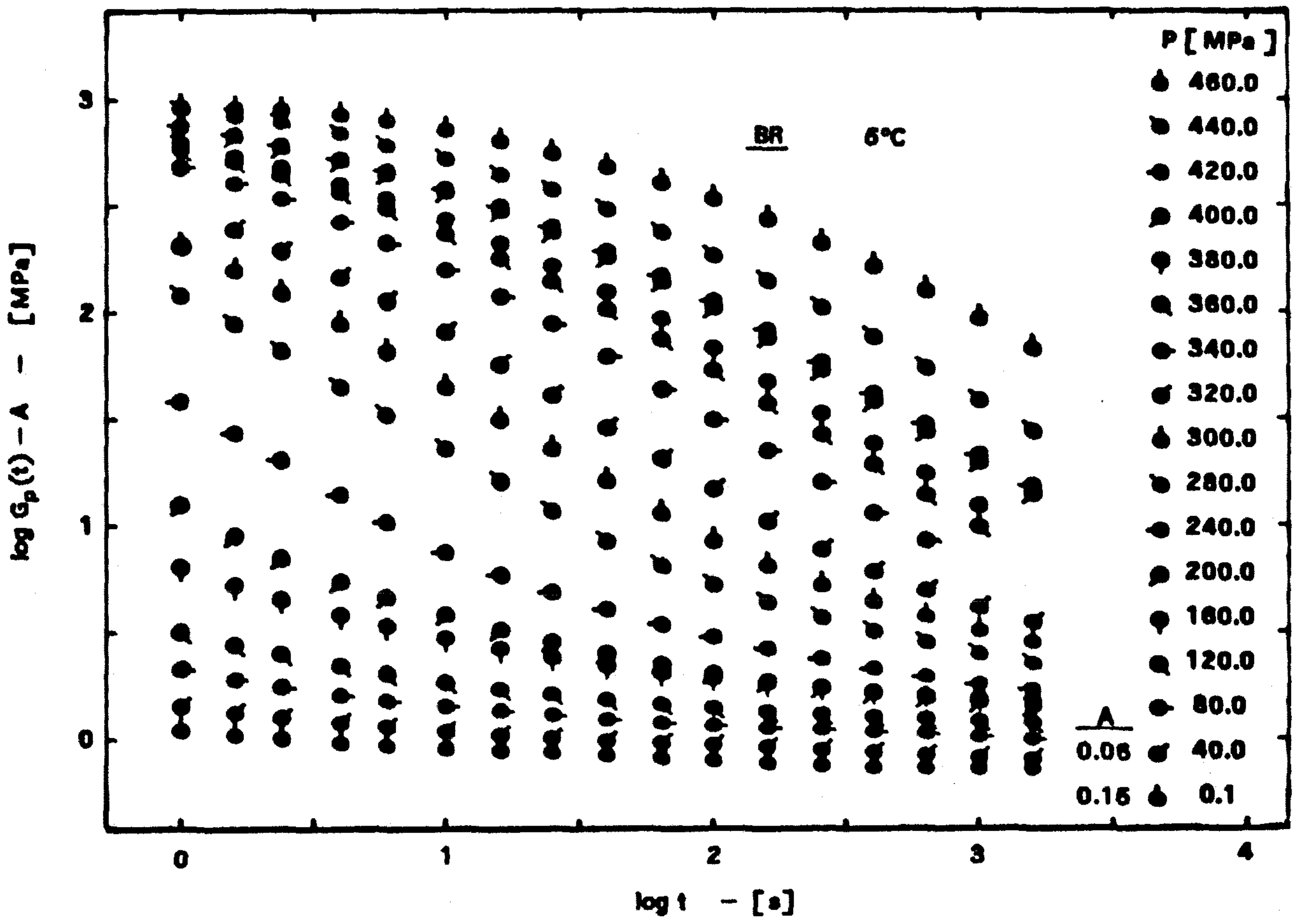

Figure 7. Butadiene rubber shear modulus $G_p(t)$ at 5^oC and pressures indicated.

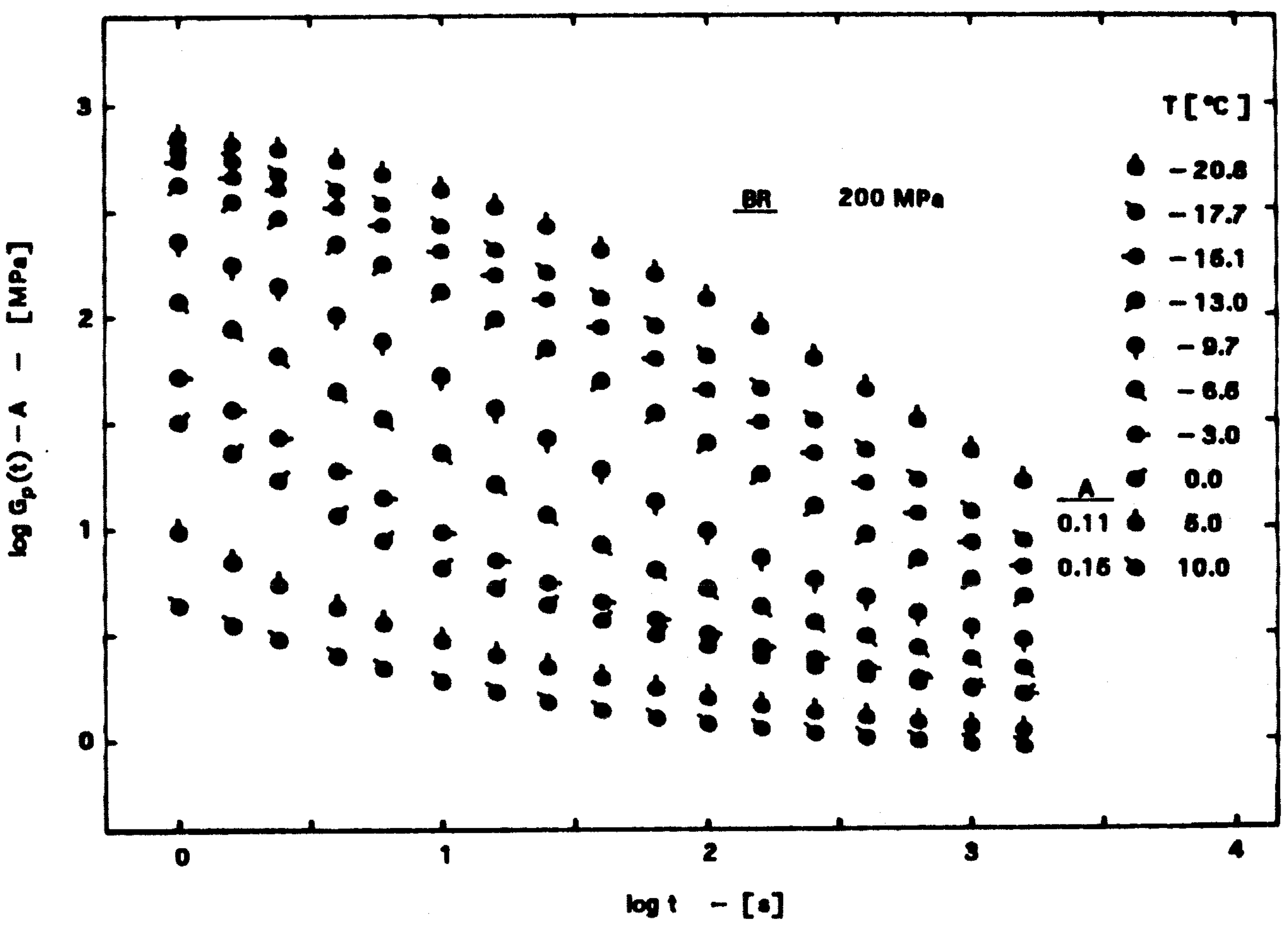

Figure 8. Butadiene rubber shear modulus $G_p(t)$ at 200 MPa and temperatures indicated.

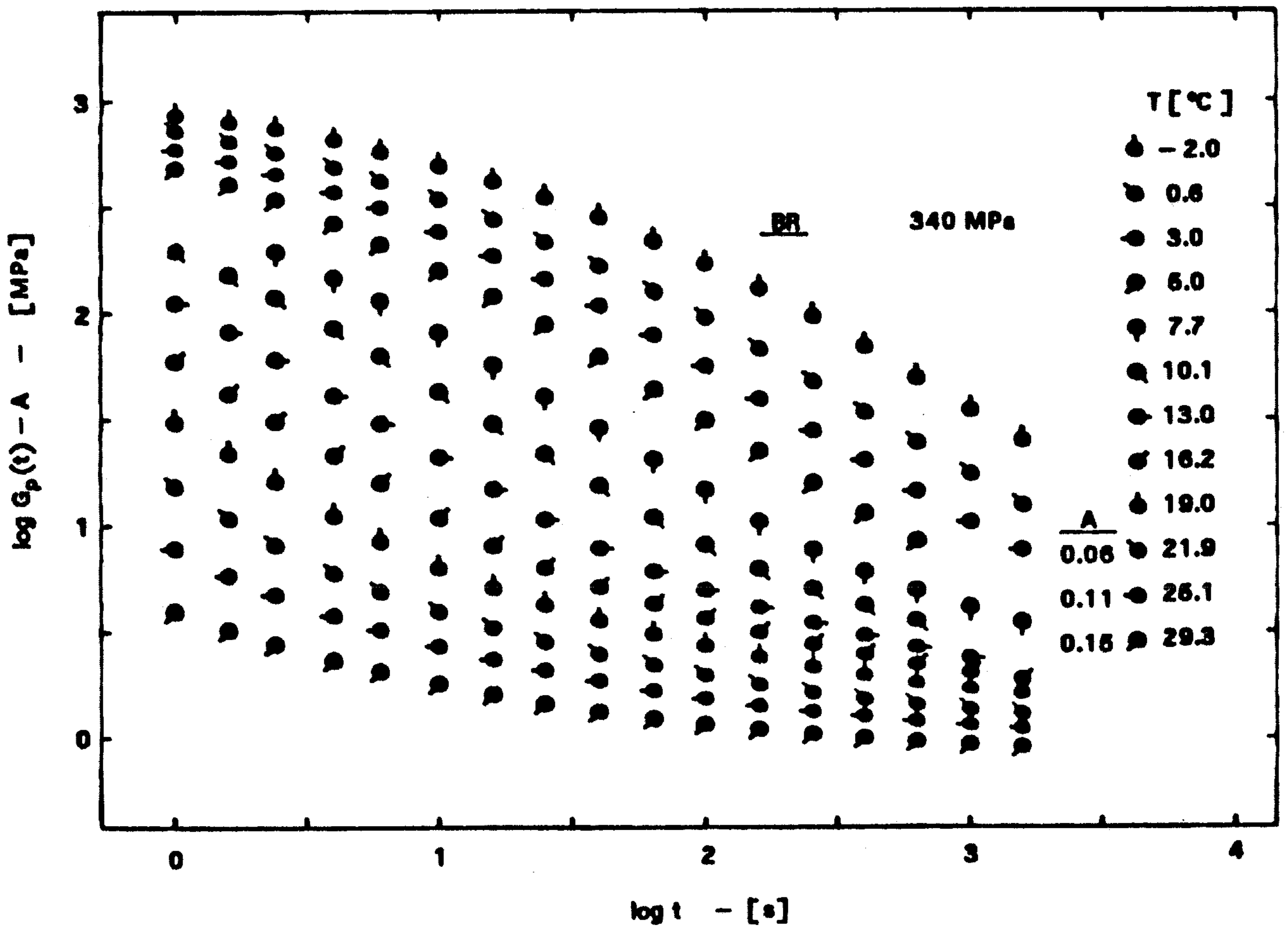

Figure 9. Butadiene rubber shear modulus $G_p(t)$ at 340 MPa and temperatures indicated.

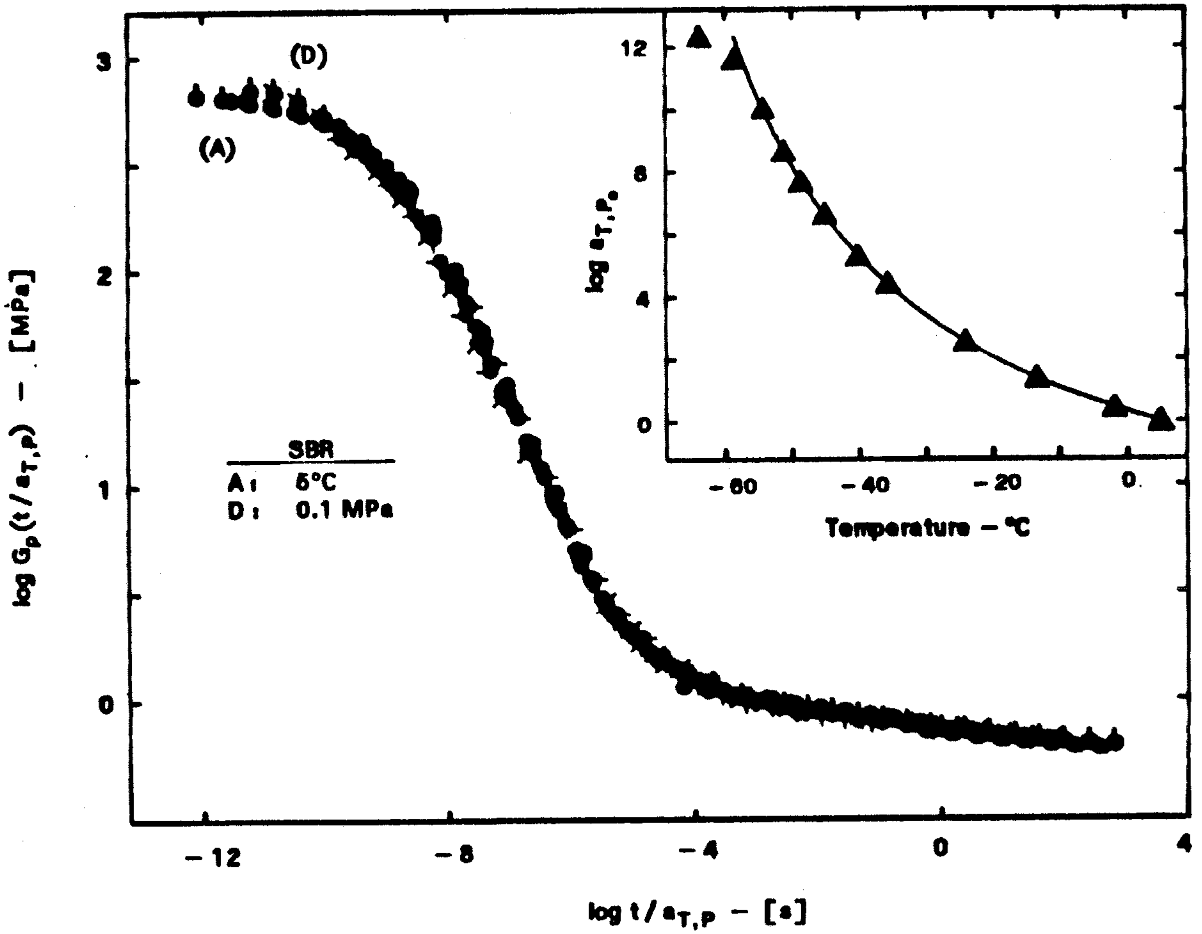

Figure 10. Styrene-butadiene rubber mastercurves. Shear modulus $G_p(t)$ reduced by shift factors from inset and Figures 14.

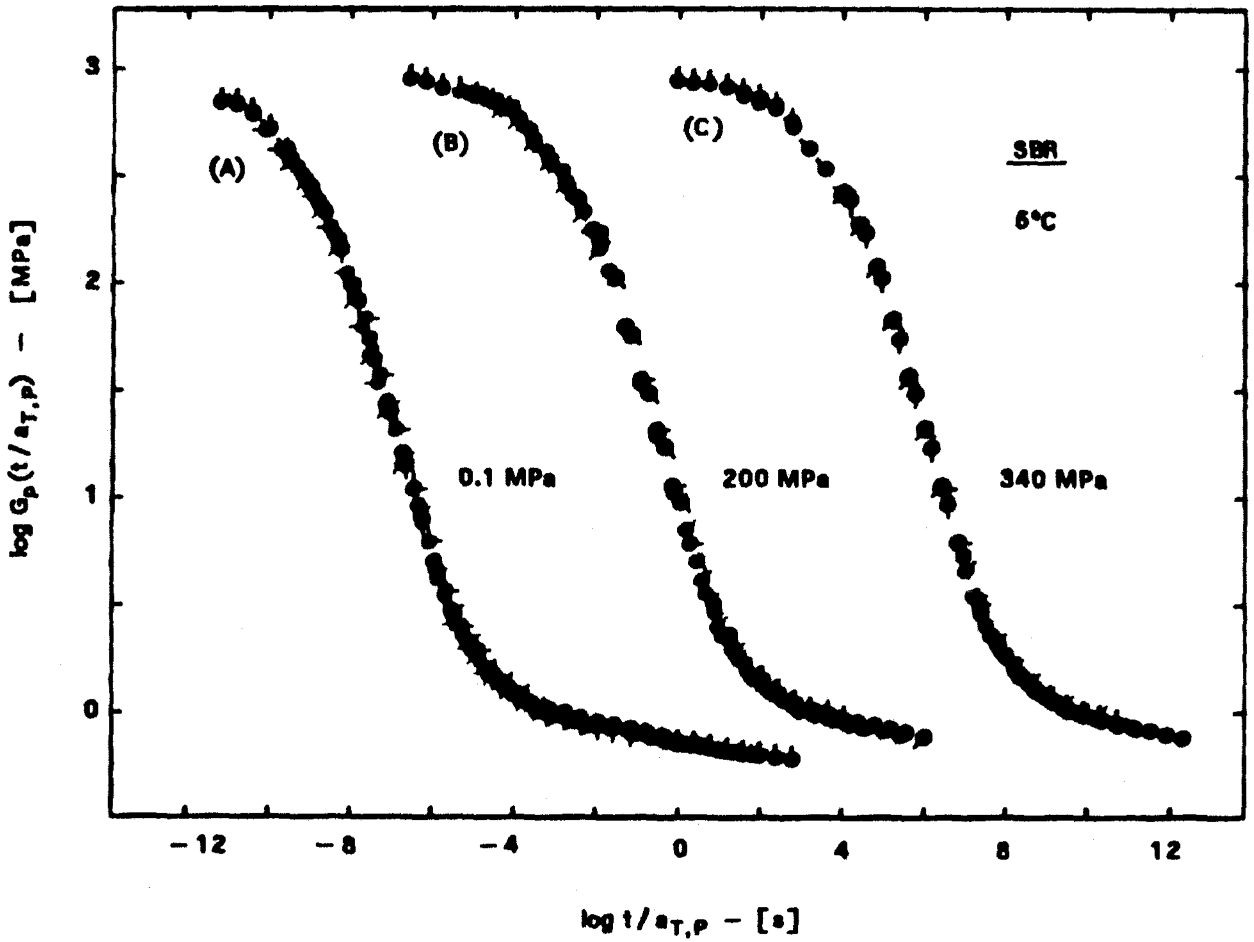

Figure 11. Styrene-butadiene rubber mastercurves. Shear modulus $G_p(t)$ reduced by shift factors from Figures 14 and 15.

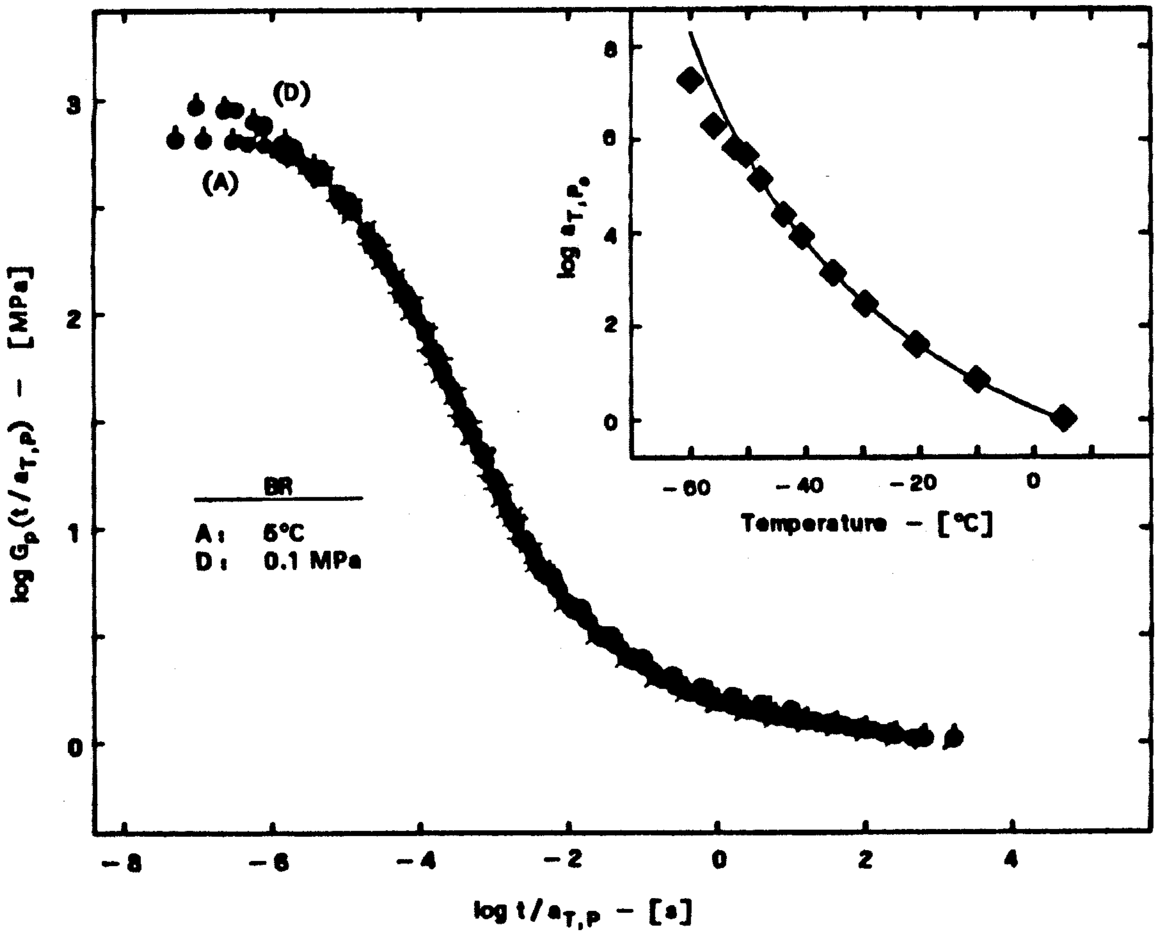

Figure 12. Styrene-butadiene rubber mastercurves. Shear modulus $G_p(t)$ reduced by shift factors from inset and from Figure 16.

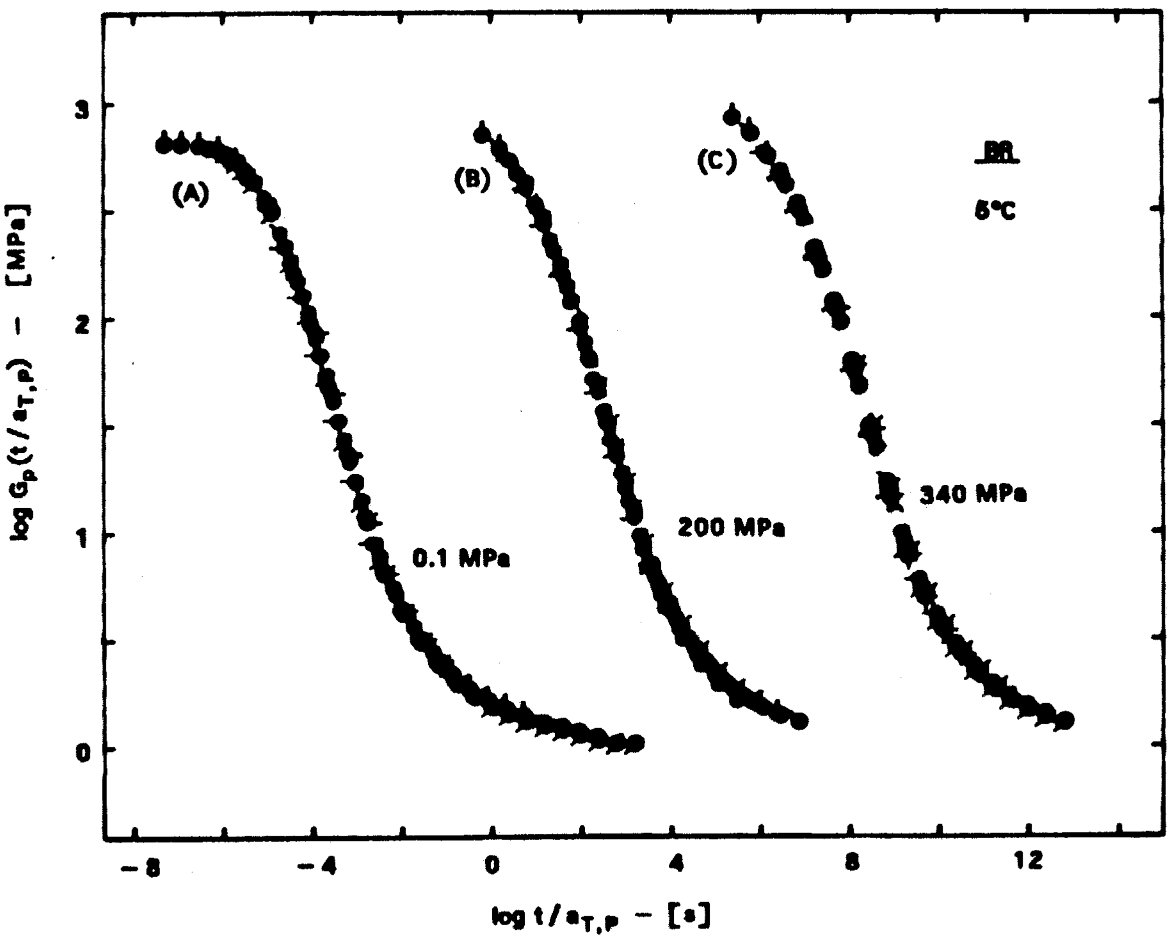

Figure 13. Styrene-butadiene rubber mastercurves. Shear modulus $G_p(t)$ reduced by shift factors from Figures 16 and 17.

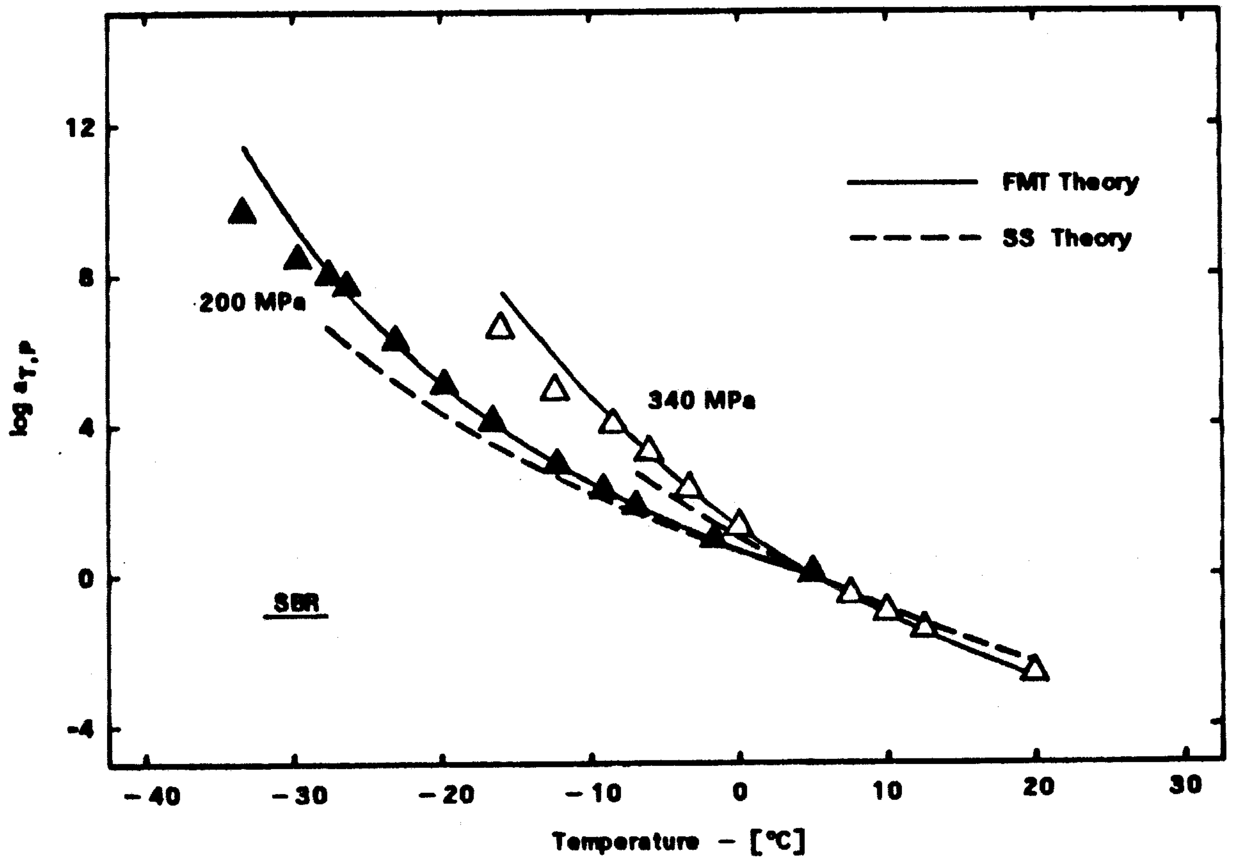

Figure 14. Styrene-butadienne rubber temperature dependence of shift factor log $a_{T,P}$ at high pressures.

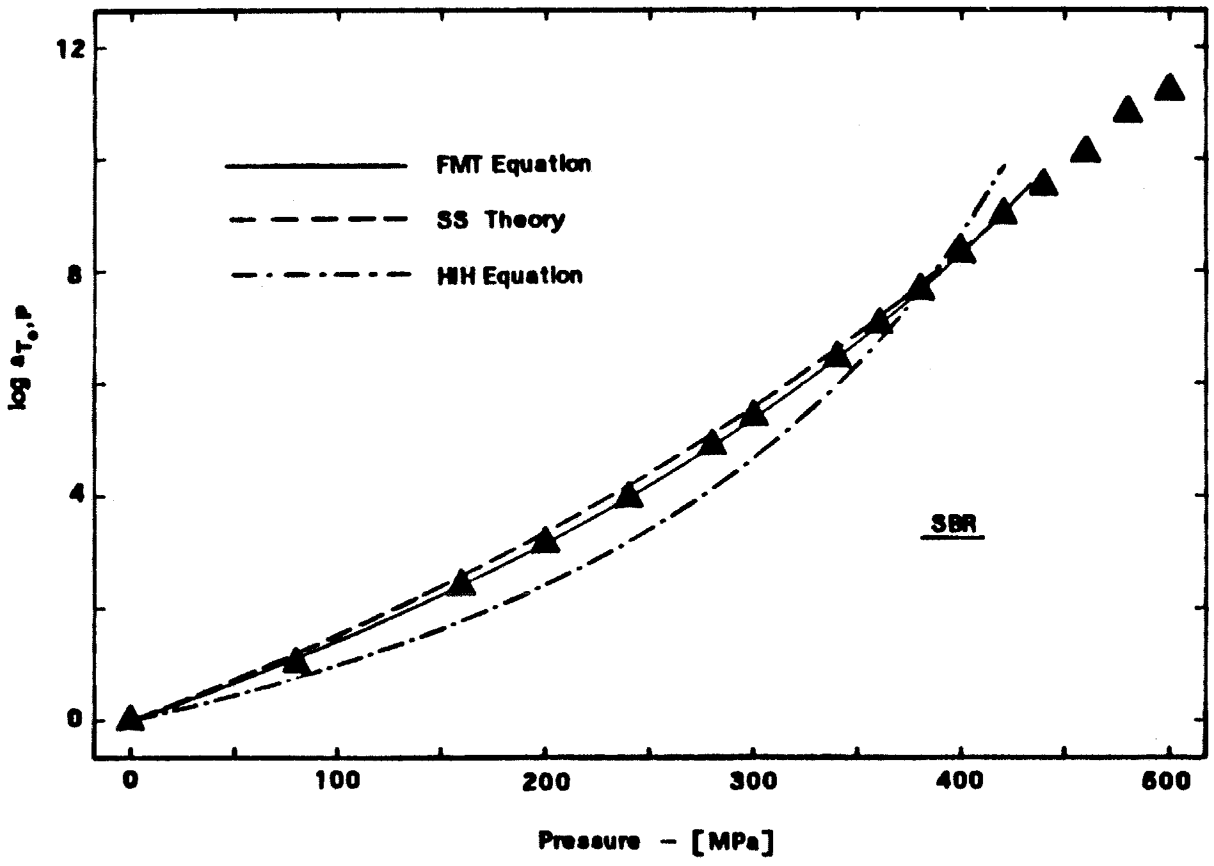

Figure 15. Styrene-butadiene rubber pressure dependence of shift factor log $a_{T_o,P}$ at 5°C.

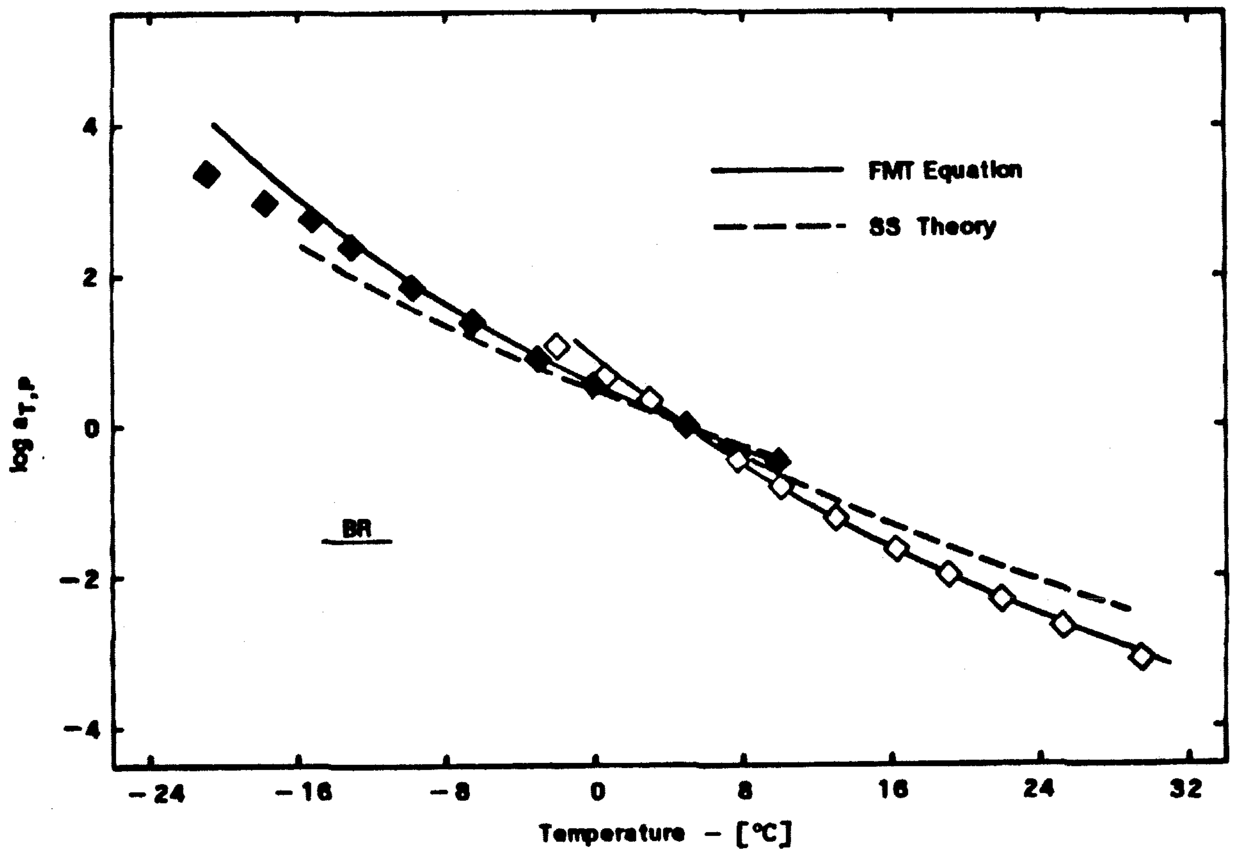

Figure 16. Butadiene rubber temperature dependence of shift factor log $a_{T,P}$ at high pressures.

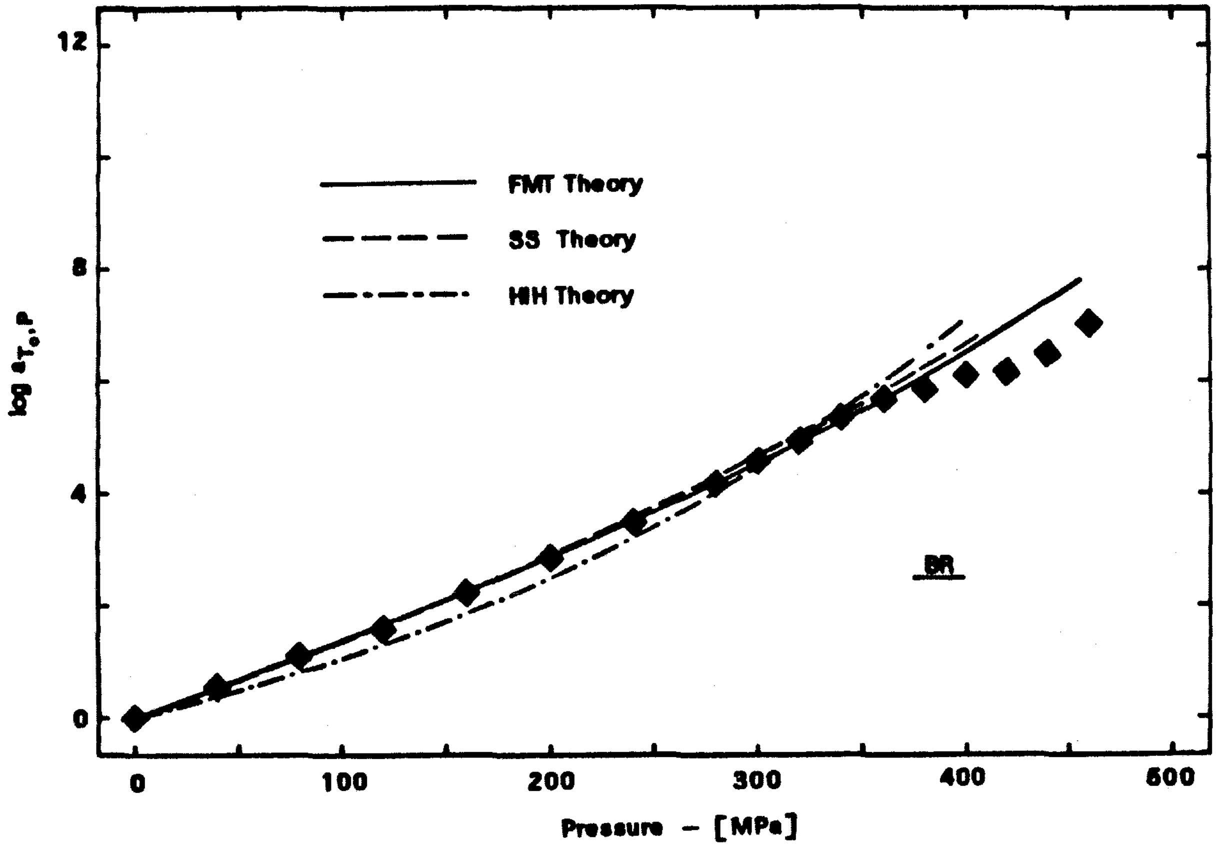

Figure 17. Butadiene rubber pressure dependence of shift factor log $a_{T_O,P}$ at 5°C.

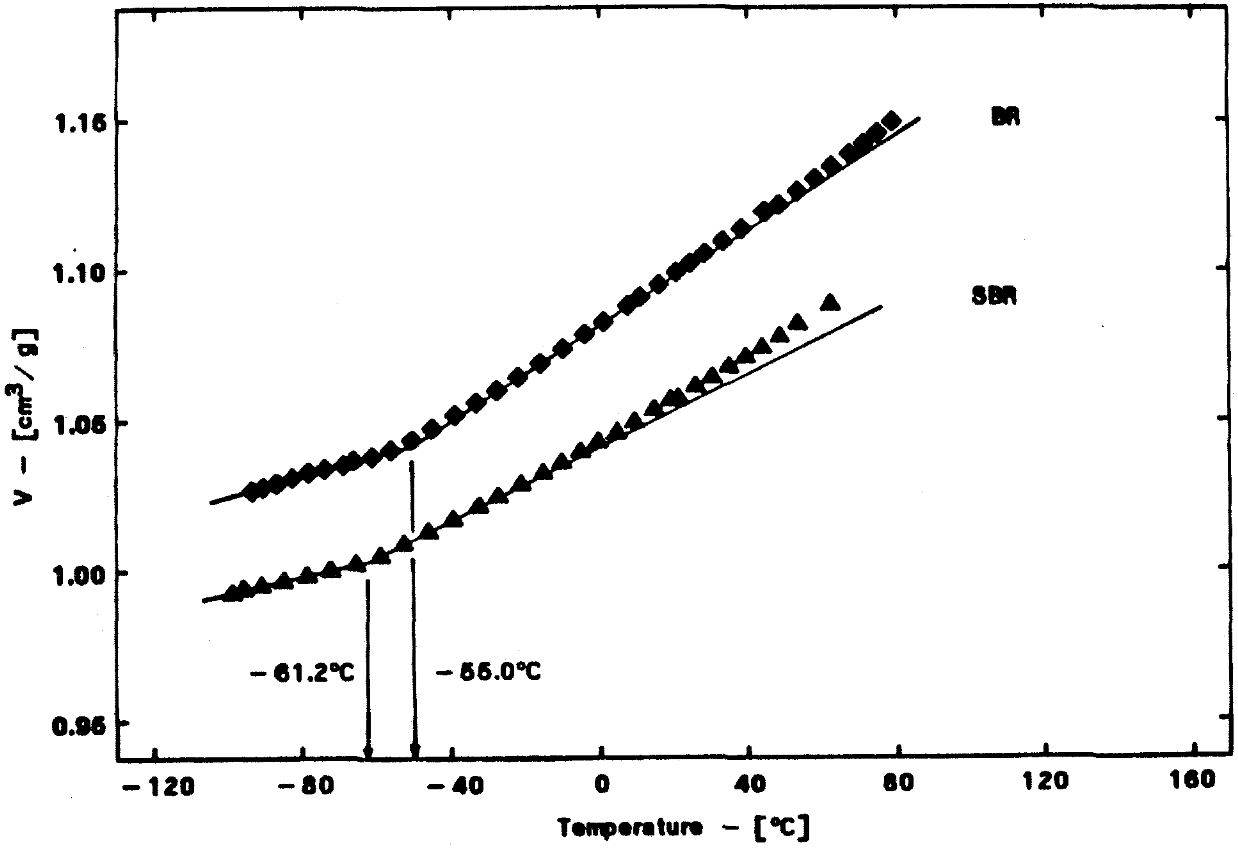

Figure 18. Thermal expansion of styrene-butadiene and butadiene rubbers.

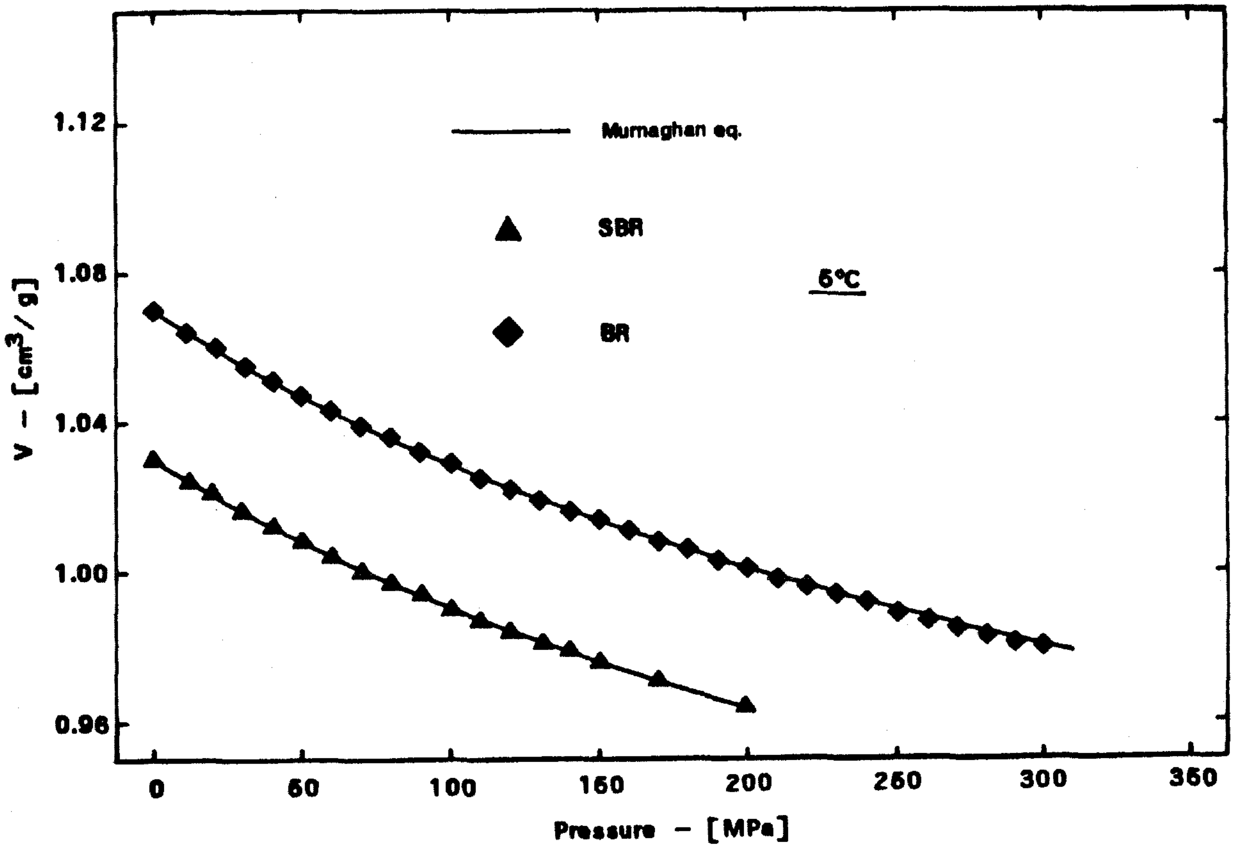

Figure 19. Bulk compression of styrene-butadiene and butadiene rubbers.

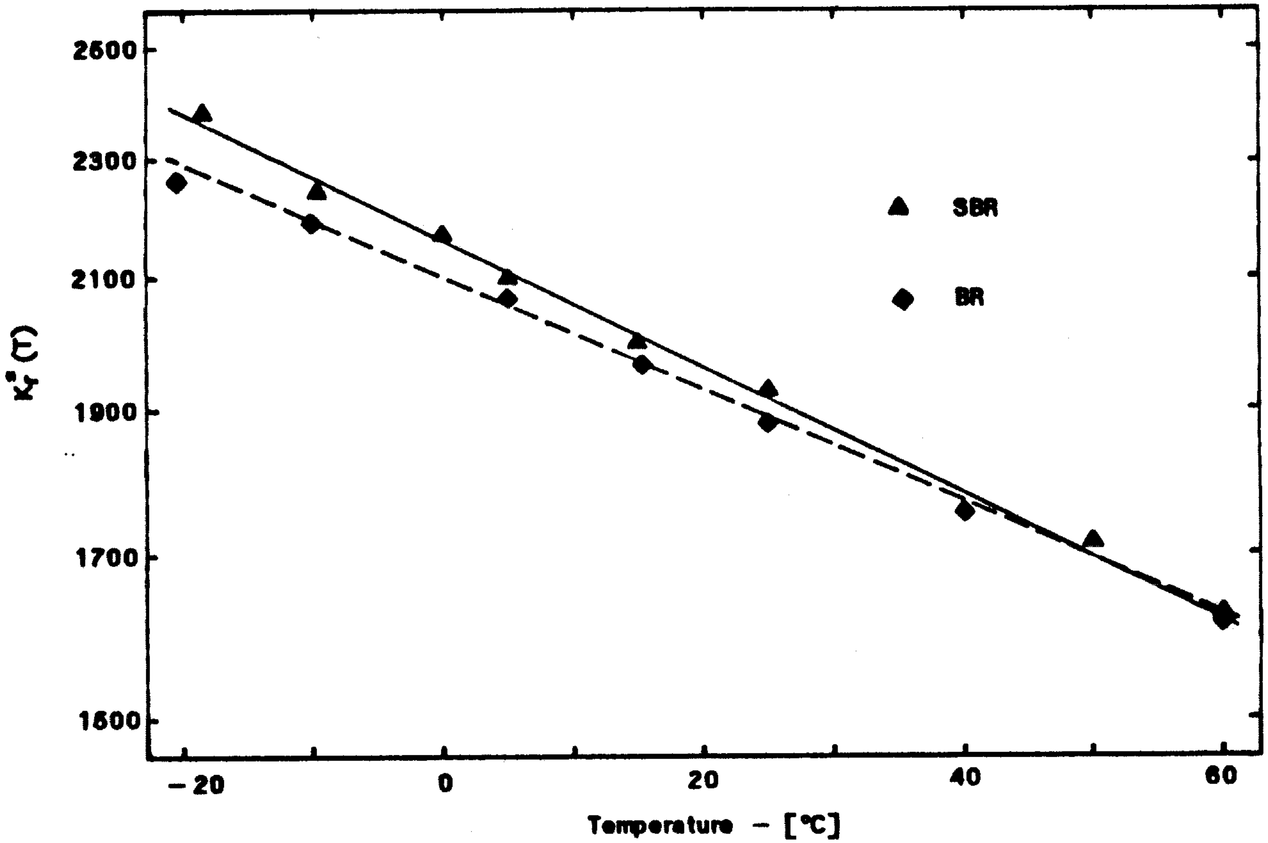

Figure 20. Temperature dependence of bulk modulus of styrene-butadiene and butadiene rubbers.

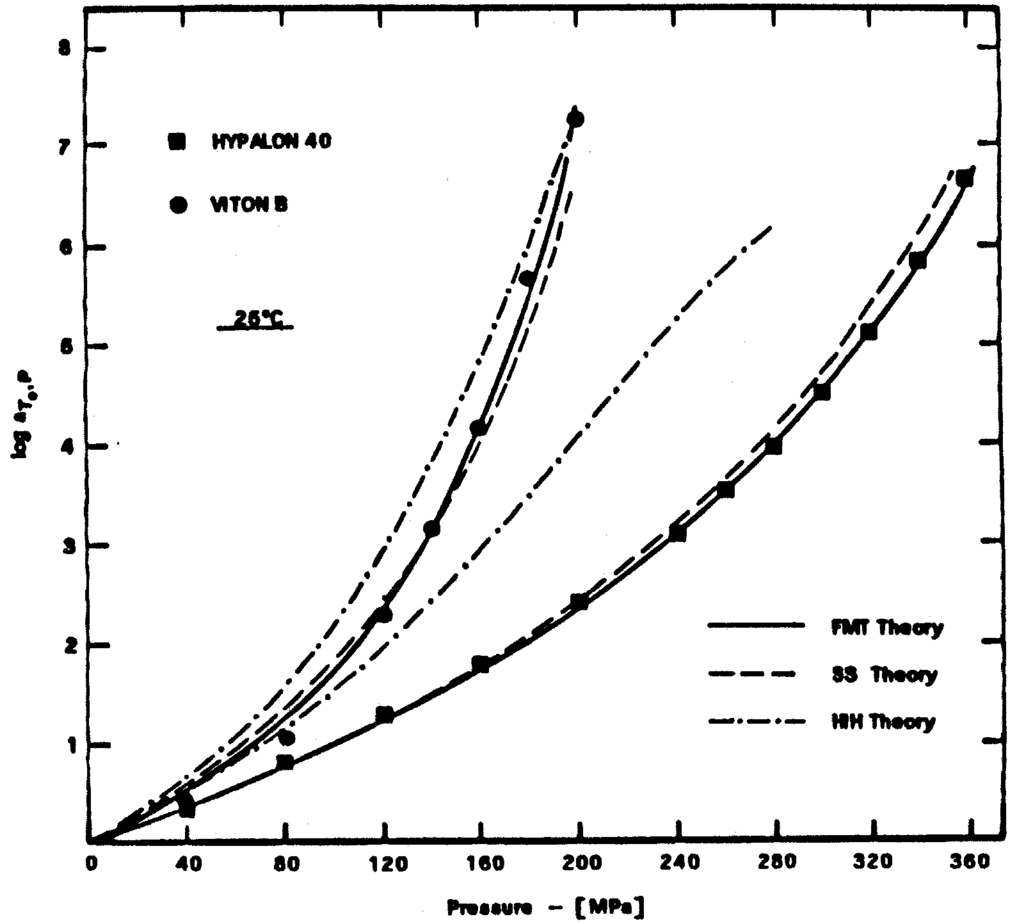

Figure 21. Pressure dependence of the shift factor log $a_{T_0,P}$ for Hypalon 40 and Viton B at 25°C.

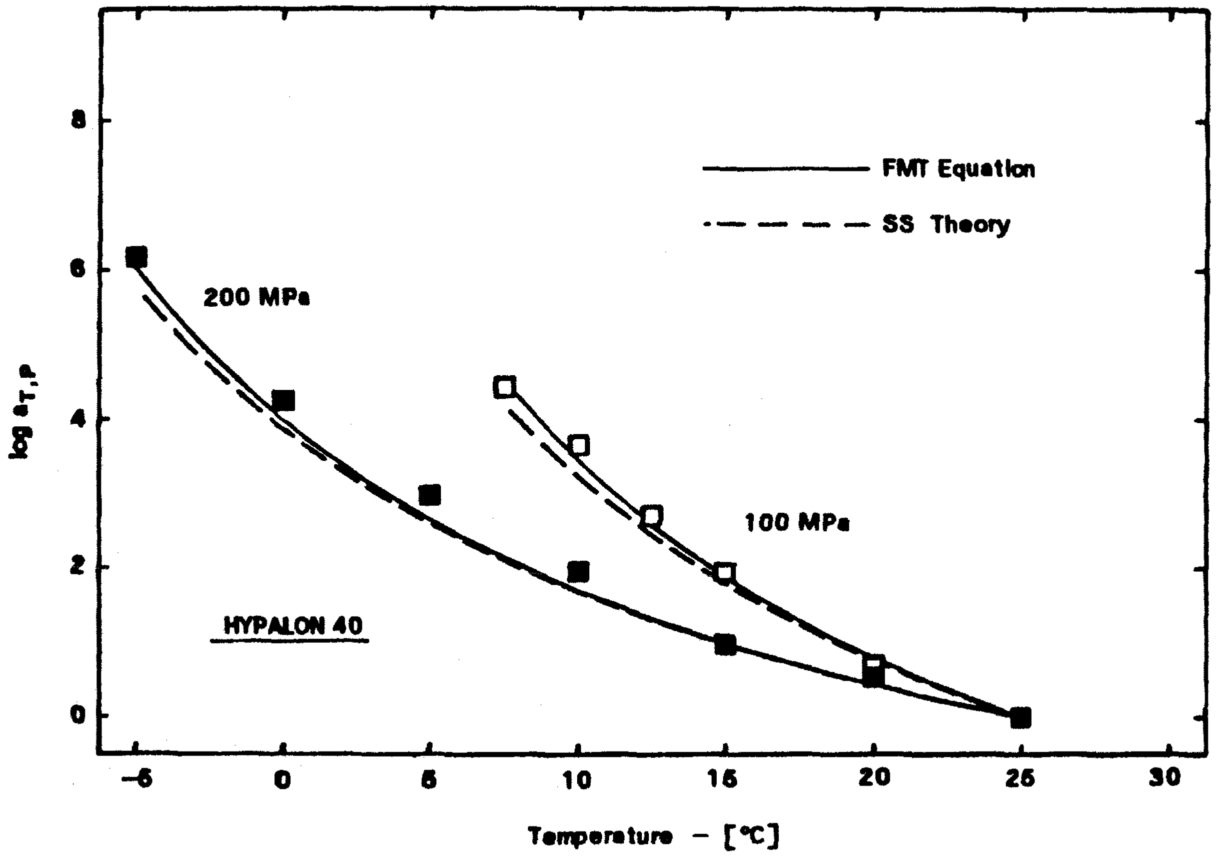

Figure 22. Temperature dependence of the shift factor log $a_{T,P}$ for Hypalon 40 at high pressures.

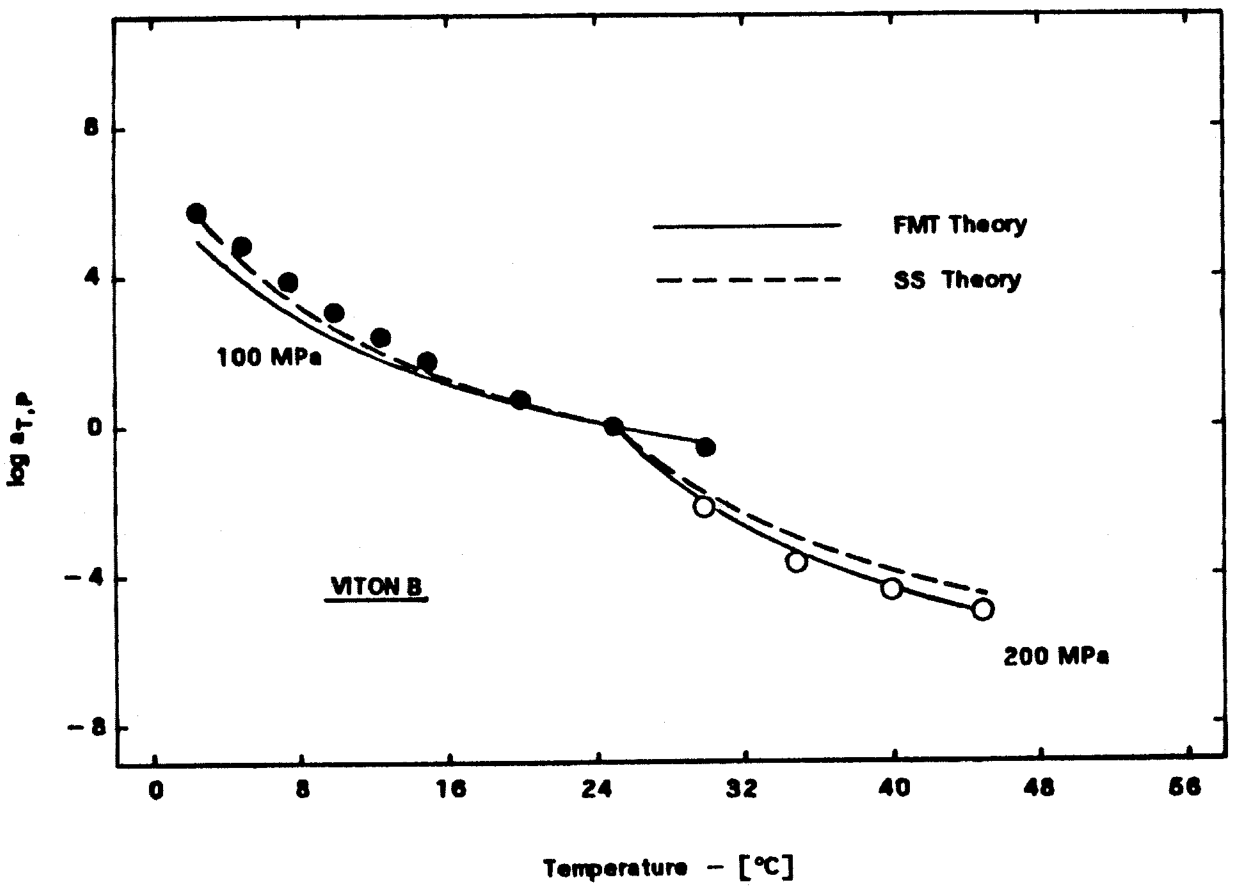

Figure 23. Temperature dependence of the shift factor log $a_{T,P}$ for Viton B at high pressures.

APPENDICES

Appendix A

Plots of the three cases of the Ferry-Stratton equation

Shown below are the plots mentioned at the end of Chapter 2, the three cases for the Ferry-Stratton equation. As mentioned previously, the fit is poor in all cases and is included only for the sake of completeness. Since the torsional data have become available, plots are also shown for SBR and BR. Again, the agreement with the data is very poor.

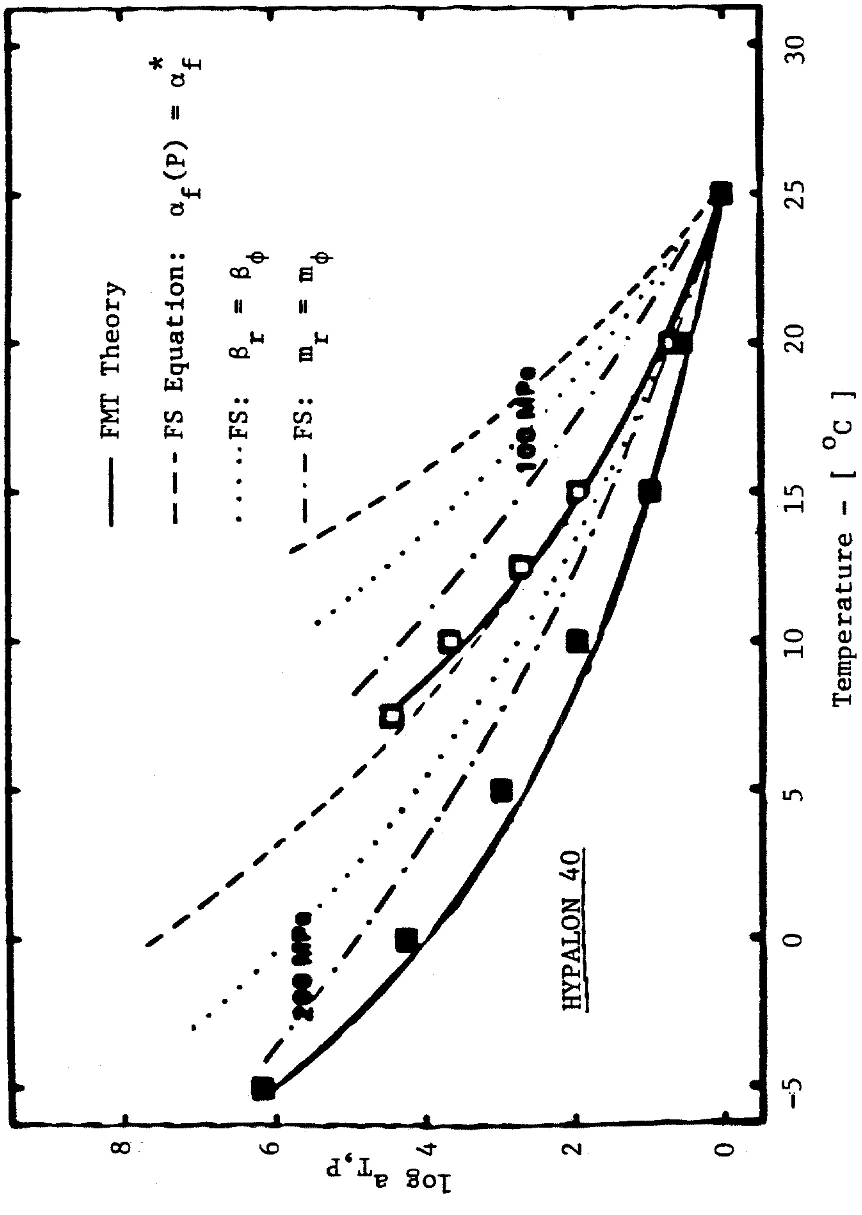

Figure 1. Shift factors for Hypalon 40 at high pressures.

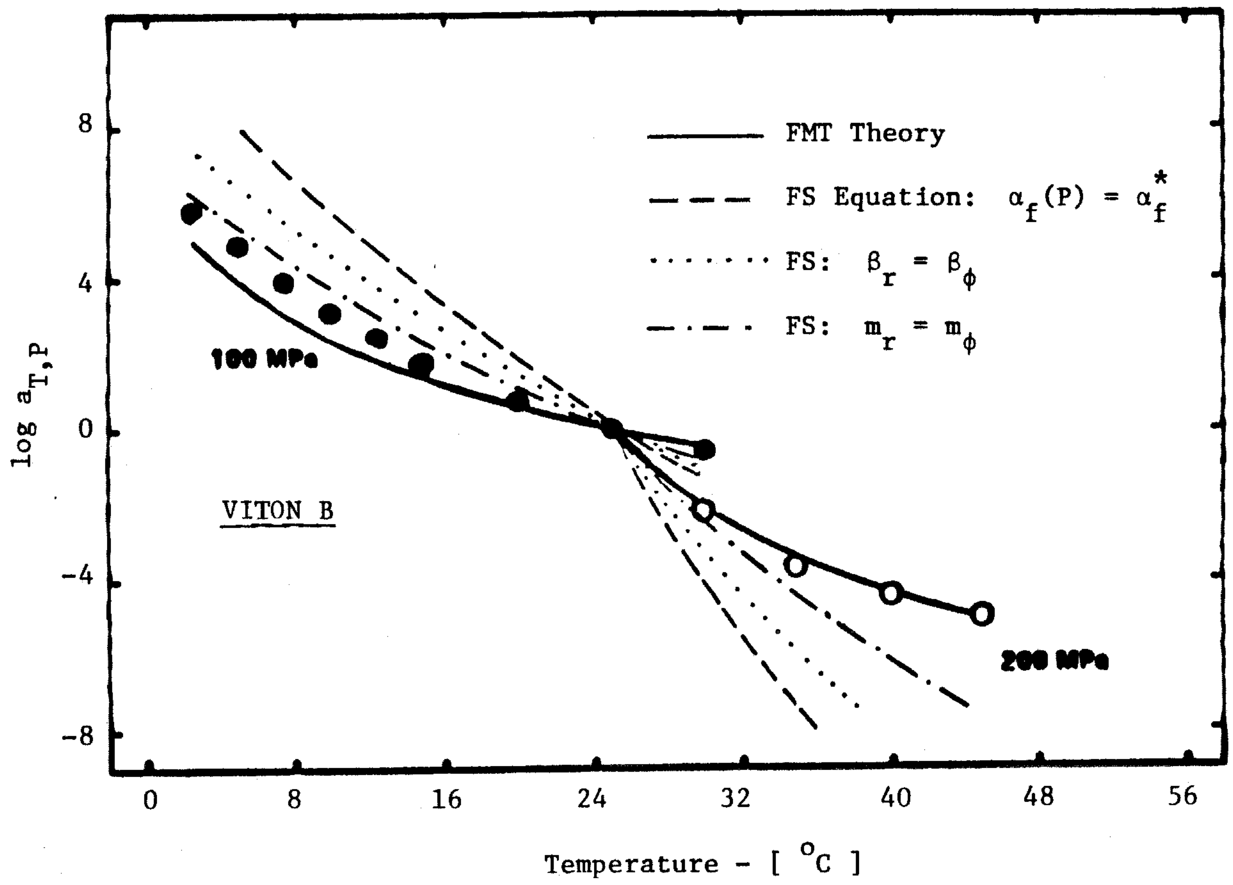

Figure 2. Shift factors for Viton B at high pressures.

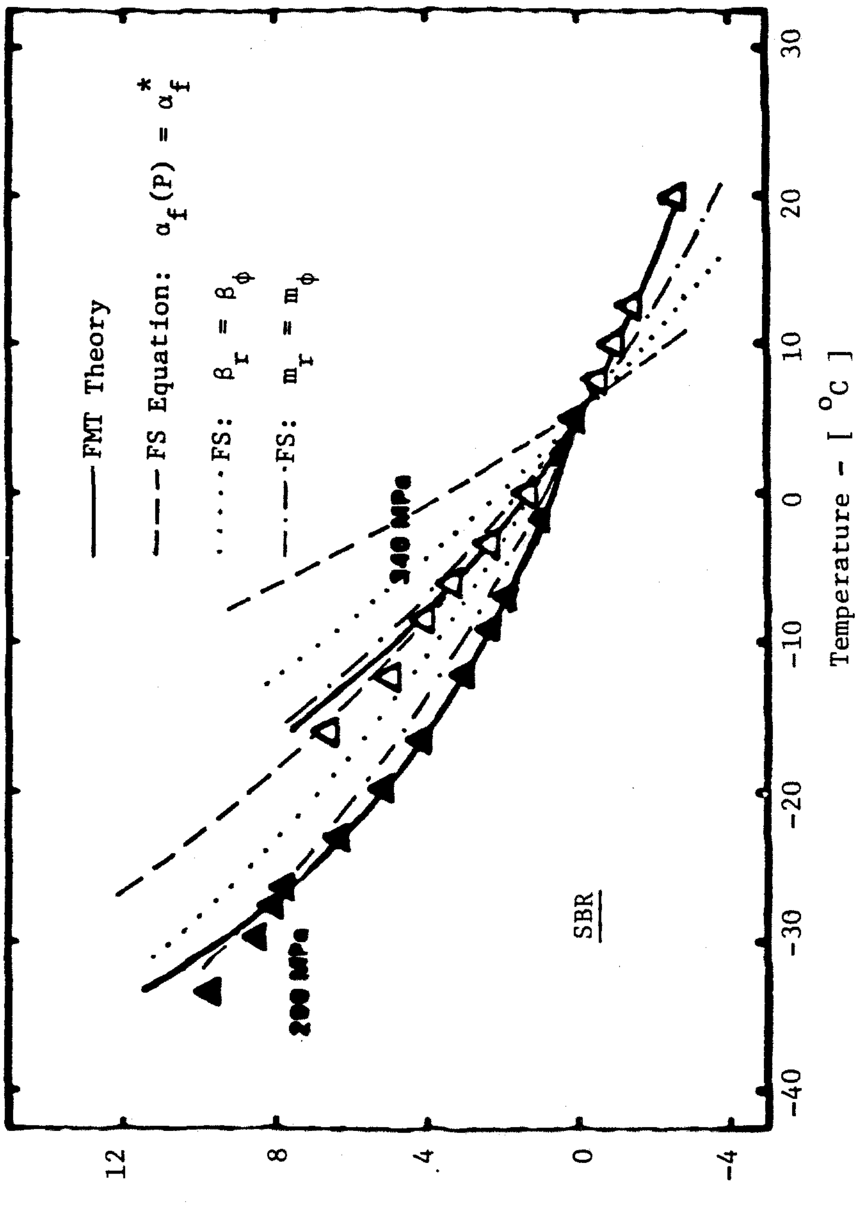

Figure 3. Shift factors for SBR at high pressures.

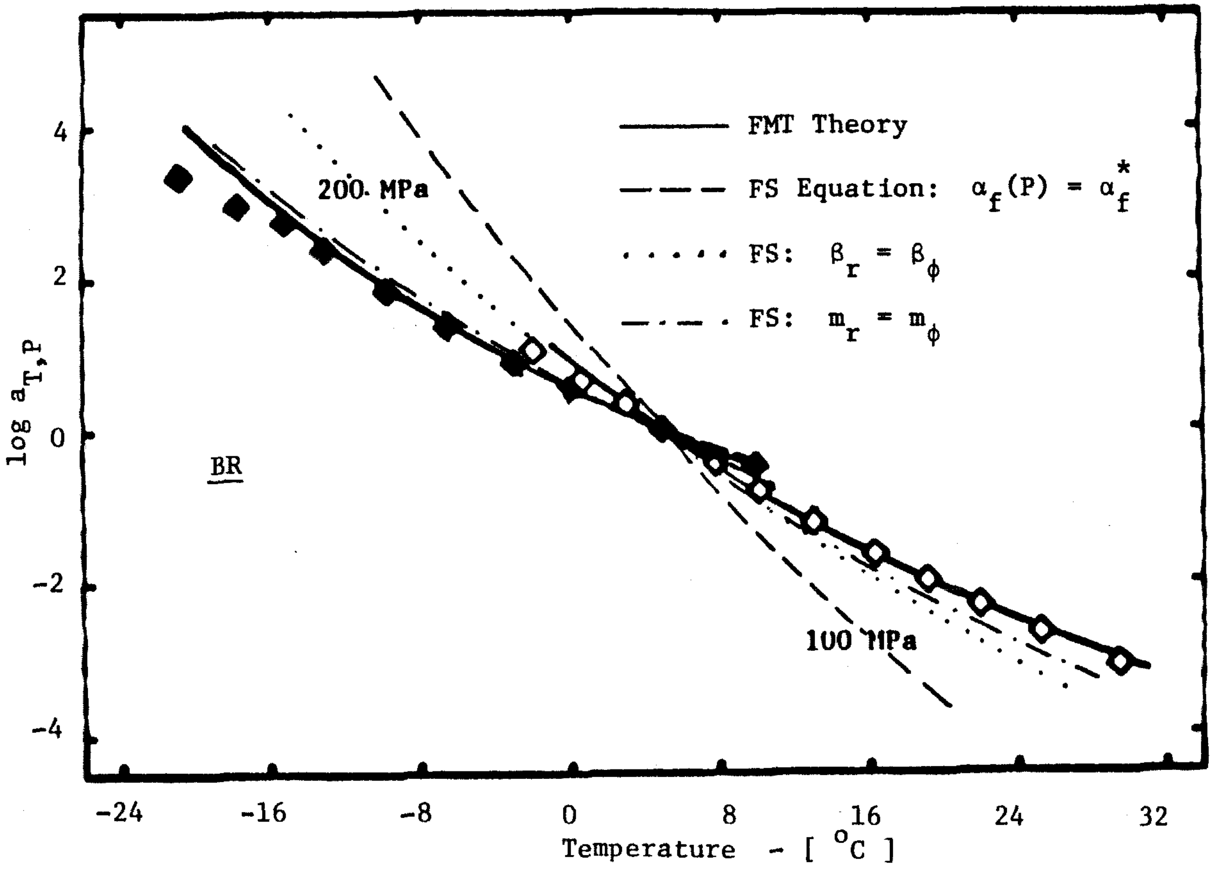

Figure 4. Shift factors for butadiene rubber at high pressures.

Appendix B

Derivation of equations 9 of Chapter 3

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

$$V(P) = V_o + \left.\frac{\partial V(P)}{\partial P}\right|_{P=0} P + \left.\frac{\partial^2 V(P)}{\partial P^2}\right|_{P=0} P^2 + \ldots$$

For the Tait equation this takes the form

$$V(P) = V_o\left[1 - \frac{1}{K_t^*} P + \frac{k_t}{2(K_t^*)^2} P^2 \mp \ldots\right]$$

while the Murnaghan equation yields

$$V(P) = V_o\left[1 - \frac{V}{V_o K^*} P + \frac{(k+1)V}{2V_o (K^*)^2} P^2 \mp \ldots\right]$$

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

Appendix C

Improved form of the HIH equation

In deriving their equation, Havlícek, et al. used an inappropriate assumption concerning the pressure dependence of the expansivity. The following derivation yields a better form of the temperature dependence.

According to the Adam-Gibbs theory the probability of a cooperative configurational rearrangement is

$$W(T,P) = A\exp[\,-m/TS_c(T,P)] \tag{1}$$

where A is a constant, m is another constant representing local topological conditions of the rearrangement and S_c is the configurational entropy of the system. Since configurational motions occur only above T_g, the differential of S_c can be written as

$$dS_c = \frac{\Delta C_p}{T}\,dT - V\Delta\alpha dP \tag{2}$$

where ΔC_p, V, and $\Delta\alpha$ have their usual meanings. The extension of the Gibbs-DiMarzio theory to high pressures (ref. 16 of Chapter 4) predicts that there is a state (T_2,P_2) at which the configurational entropy is essentially zero. Integrating eq. (2) yields

$$S_c = \Delta C_p \ln\,(T/T_2^0) - V\int_{P_2}^{P} \Delta\alpha dP \tag{3}$$

where we have taken ΔC_p, V, and $\Delta\alpha$ as independent of temperature. We select $P_2 = 0.1$ MPa ≈ 0. The corresponding temperature is T_2^0.

At this point an assumption about $\Delta\alpha(P)$ must be introduced. Havlícek, et al., assumed that $\Delta\alpha(P) = \Delta\alpha_o - aP$. However, the Murnaghan and Gee equations (see eqs. (4) and (6) of Chapter 4) determine a different relationship. By Murnaghan's equation (taking $P_o = 0$) we have

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

Then by introducing Gee's equation we obtain

$$\alpha(P) = \frac{1}{V}\frac{dV}{dT} = \alpha^* - \frac{\beta P}{K^*(T) + kP} \tag{5}$$

where α^* is the thermal expansion coefficient at zero pressure. Assuming eq. (5) is true of the rubber and the glass (this has been verified experimentally in Chapter 3 as well as in other investigations) then

$$S_c = \Delta C_p \ln (T/T_2^o) - V\Bigg[\Delta\alpha^* - \frac{\beta_r^*}{k_r^2}[Pk_r - K_{ro}^* \ln (K_{ro}^* + k_r P)] \tag{6}$$

$$+ \frac{\beta_g^*}{k_g^2}[Pk_g - K_{go}^* \ln (K_{go}^* + k_g P)]\Bigg]$$

The quantity $h(T,P)$ (eq. (11)) is simply the reciprocal of the product of the temperature and the configurational entropy. This form seems to fit the data as well as the FMT equation, but it is certainly no more convenient to use and is perhaps misleading, since, as noted earlier, ΔC_p must be determined by a fit to the shift data and does not agree with experimentally determined values.

Appendix D

Experimental Data

The following pages contain data for the torsional relaxation experiments described in Chapter 4. The data sets, or runs, are arranged in isothermal and isobaric groups.

The run number corresponds to an entry in the laboratory notebook. The angle shown is the angle, in radians, through which the specimen was twisted. The diameter and length are that of the cylindrical specimen, in centimeters. The ratio of the specific volume at the experimental conditions to the volume at the reference conditions is provided so that there is sufficient information to apply the rubber elasticity and density corrections. However, the modulus shown in the tables is the uncorrected modulus, not $G_p(t)$ shown in Figures 2 - 9 of Chapter 4. The units of $G(t)$ are Pascals which also differs from the figures of Chapter 4. The units of time are seconds.

RUN 253 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 280.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.917838

log G(t)	log t	log G(t)	log t
8.092	0.000	6.942	1.602
7.959	0.204	6.828	1.806
7.829	0.380	6.740	2.000
7.662	0.602	6.658	2.204
7.531	0.778	6.585	2.408
7.373	1.000	6.522	2.602
7.223	1.204	6.468	2.798
7.080	1.398	6.416	3.000
		6.368	3.200

RUN 248 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 160.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.943234

log G(t)	log t	log G(t)	log t
6.782	0.000	6.321	1.602
6.697	0.204	6.290	1.806
6.632	0.380	6.265	2.000
6.558	0.602	6.242	2.204
6.508	0.778	6.221	2.408
6.450	1.000	6.203	2.602
6.401	1.204	6.186	2.798
6.359	1.398	6.172	3.000
		6.160	3.200

RUN 247 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.933782

log G(t)	log t	log G(t)	log t
7.101	0.000	6.410	1.602
6.958	0.204	6.360	1.806
6.853	0.380	6.317	2.000
6.744	0.602	6.279	2.204
6.670	0.778	6.247	2.408
6.587	1.000	6.223	2.602
6.519	1.204	6.201	2.798
6.462	1.398	6.179	3.000
		6.160	3.200

RUN 246 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 80.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.966589

log G(t)	log t	log G(t)	log t
6.372	0.000	6.141	1.602
6.325	0.204	6.126	1.806
6.289	0.380	6.114	2.000
6.252	0.602	6.104	2.204
6.228	0.778	6.095	2.408
6.201	1.000	6.085	2.602
6.180	1.204	6.075	2.798
6.160	1.398	6.062	3.000
		6.049	3.200

RUN 103 MATERIAL SBR

TEMPERATURE: -63.6 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.955847

log G(t)	log t	log G(t)	log t
8.689	0.176	8.618	1.778
8.683	0.398	8.602	2.000
8.675	0.602	8.570	2.204
8.676	0.778	8.545	2.380
8.662	1.000	8.508	2.611
8.652	1.204	8.467	2.820
8.642	1.398	8.426	3.009
8.631	1.602	8.378	3.183

RUN 104 MATERIAL SBR

TEMPERATURE: -58.6 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.1997 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.958987

log G(t)	log t	log G(t)	log t
8.680	0.079	8.567	1.602
8.671	0.204	8.543	1.778
8.663	0.380	8.508	2.000
8.650	0.602	8.471	2.204
8.640	0.778	8.423	2.408
8.625	1.000	8.375	2.602
8.607	1.204	8.312	2.806
8.589	1.398	8.249	3.000

RUN 110 MATERIAL SBR

TEMPERATURE: -54.2 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.961765

log G(t)	log t	log G(t)	log t
8.569	0.204	8.170	1.602
8.542	0.380	8.082	1.778
8.497	0.602	7.958	2.000
8.448	0.778	7.834	2.204
8.379	1.000	7.711	2.380
8.310	1.204	7.559	2.611
8.260	1.398	7.432	2.799
		7.308	2.982

RUN 098 MATERIAL SBR

TEMPERATURE: -48.5 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.965406

log G(t)	log t	log G(t)	log t
7.753	0.000	6.855	1.398
7.614	0.176	6.716	1.602
7.472	0.398	6.594	1.778
7.375	0.602	6.471	2.000
7.253	0.778	6.366	2.225
7.090	1.000	6.291	2.380
6.980	1.204	6.217	2.611
		6.171	2.820

RUN 101 MATERIAL SBR

TEMPERATURE: -51.2 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.963677

log G(t)	log t	log G(t)	log t
8.282	0.000	7.363	1.602
8.211	0.176	7.250	1.778
8.122	0.398	7.091	2.000
8.004	0.602	6.970	2.225
7.897	0.778	6.862	2.380
7.770	1.000	6.724	2.611
7.616	1.204	6.586	2.820
7.481	1.398	6.477	3.009

RUN 100 MATERIAL SBR

TEMPERATURE: -40.1 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.970756

log G(t)	log t	log G(t)	log t
6.138	0.602	5.954	1.778
6.105	0.778	5.932	2.000
6.064	1.000	5.915	2.204
6.029	1.204	5.899	2.398
5.999	1.398	5.883	2.602
5.973	1.602	5.865	2.806
		5.853	3.000

RUN 113 MATERIAL SBR

TEMPERATURE: -45.2 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.967514

log G(t)	log t	log G(t)	log t
7.073	0.000	6.267	1.398
6.957	0.204	6.220	1.602
6.846	0.380	6.173	1.778
6.690	0.602	6.107	2.000
6.567	0.778	6.076	2.225
6.437	1.000	6.041	2.398
6.355	1.204	6.016	2.602

RUN 102 MATERIAL SBR

TEMPERATURE: -24.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.981099

log G(t)	log t	log G(t)	log t
5.906	0.000	5.848	1.398
5.901	0.204	5.837	1.602
5.895	0.380	5.829	1.778
5.885	0.602	5.820	2.000
5.877	0.778	5.809	2.225
5.867	1.000	5.802	2.380
5.856	1.204	5.795	2.611
		5.787	2.820

RUN 108 MATERIAL SBR

TEMPERATURE: -35.6 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.973630

log G(t)	log t	log G(t)	log t
5.978	0.204	5.907	1.602
5.973	0.380	5.895	1.778
5.962	0.602	5.883	2.000
5.951	0.778	5.870	2.225
5.940	1.000	5.862	2.380
5.927	1.204	5.849	2.611
5.918	1.398	5.838	2.820
		5.828	3.009

RUN 106 MATERIAL SBR

TEMPERATURE: -1.8 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.995519

log G(t)	log t	log G(t)	log t
5.817	0.204	5.773	1.602
5.811	0.380	5.769	1.778
5.804	0.602	5.762	2.000
5.798	0.778	5.757	2.225
5.791	1.000	5.753	2.380
5.784	1.204	5.747	2.611
5.779	1.398	5.743	2.820
		5.740	3.009

RUN 109 MATERIAL SBR

TEMPERATURE: -13.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.988195

log G(t)	log t	log G(t)	log t
5.854	0.000	5.797	1.602
5.849	0.204	5.791	1.778
5.844	0.380	5.781	2.000
5.836	0.602	5.777	2.225
5.828	0.778	5.772	2.380
5.818	1.000	5.766	2.611
5.811	1.204	5.761	2.820
5.804	1.398	5.756	3.009
		5.751	3.193

RUN 179 MATERIAL SBR

TEMPERATURE: -33.3 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.910843

log G(t)	log t	log G(t)	log t
8.903	0.000	8.834	1.398
8.897	0.204	8.821	1.602
8.887	0.380	8.816	1.778
8.870	0.602	8.794	2.000
8.859	0.778	8.772	2.201
8.849	1.000	8.758	2.401
8.846	1.204	8.725	2.600
		8.676	2.800

RUN 117 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 1.00000

log G(t)	log t	log G(t)	log t
5.835	0.000	5.788	1.602
5.831	0.204	5.784	1.778
5.826	0.380	5.779	2.000
5.818	0.602	5.774	2.201
5.813	0.778	5.770	2.401
5.807	1.000	5.765	2.600
5.800	1.204	5.763	2.800
5.794	1.398	5.758	3.003

RUN 181 MATERIAL SBR

TEMPERATURE: -27.6 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.914230

log G(t)	log t	log G(t)	log t
8.839	0.000	8.601	1.398
8.820	0.204	8.571	1.602
8.812	0.380	8.522	1.778
8.795	0.602	8.481	2.000
8.779	0.778	8.418	2.201
8.727	1.000	8.344	2.401
8.672	1.204	8.284	2.600
		8.197	2.800

RUN 171 MATERIAL SBR

TEMPERATURE: -29.6 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.913034

log G(t)	log t	log G(t)	log t
8.841	0.204	8.659	1.602
8.823	0.380	8.610	1.778
8.813	0.602	8.566	2.000
8.796	0.778	8.512	2.201
8.771	1.000	8.468	2.401
8.752	1.204	8.400	2.600
8.714	1.398	8.334	2.800

RUN 176 MATERIAL SBR

TEMPERATURE: -23.1 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.916933

log G(t)	log t	log G(t)	log t
8.364	0.602	7.633	2.000
8.306	0.778	7.501	2.204
8.218	1.000	7.377	2.408
8.124	1.204	7.255	2.602
8.023	1.398	7.128	2.798
7.904	1.602	6.997	3.000
7.766	1.806	6.873	3.200

RUN 170 MATERIAL SBR

TEMPERATURE: -26.4 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.914957

log G(t)	log t	log G(t)	log t
8.780	0.204	8.493	1.602
8.766	0.380	8.430	1.778
8.728	0.602	8.356	2.000
8.681	0.778	8.293	2.201
8.627	1.000	8.225	2.401
8.578	1.204	8.121	2.600
8.534	1.398	8.009	2.800

RUN 304 MATERIAL SBR

TEMPERATURE: -19.8 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.918912

log G(t)	log t	log G(t)	log t
8.202	0.000	7.205	1.602
8.096	0.204	7.073	1.806
7.995	0.380	6.951	2.000
7.850	0.602	6.821	2.204
7.729	0.778	6.679	2.408
7.583	1.000	6.565	2.602
7.458	1.204	6.478	2.798
7.337	1.398	6.390	3.000
		6.337	3.200

RUN 305 MATERIAL SBR

TEMPERATURE: -16.5 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.920896

log G(t)	log t	log G(t)	log t
7.528	0.000	6.533	1.602
7.403	0.204	6.418	1.806
7.294	0.380	6.339	2.000
7.150	0.602	6.283	2.204
7.036	0.778	6.231	2.408
6.897	1.000	6.175	2.602
6.766	1.204	6.137	2.798
6.631	1.398	6.108	3.000
		6.074	3.200

RUN 162 MATERIAL SBR

TEMPERATURE: -9.1 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.925334

log G(t)	log t	log G(t)	log t
6.460	0.000	6.083	1.602
6.374	0.204	6.062	1.778
6.328	0.380	6.035	2.000
6.274	0.602	6.013	2.225
6.218	0.778	6.006	2.380
6.173	1.000	5.998	2.611
6.143	1.204	5.986	2.795
6.109	1.398	5.972	3.009
		5.961	3.193

RUN 165 MATERIAL SBR

TEMPERATURE: -12.2 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.923481

log G(t)	log t	log G(t)	log t
6.838	0.000	6.159	1.602
6.714	0.204	6.132	1.806
6.601	0.380	6.096	2.000
6.477	0.602	6.067	2.204
6.388	0.778	6.042	2.408
6.317	1.000	6.020	2.602
6.266	1.204	5.997	2.798
6.212	1.398	5.982	3.000
		5.976	3.200

RUN 163 MATERIAL SBR

TEMPERATURE: -1.6 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.929875

log G(t)	log t	log G(t)	log t
6.107	0.000	5.967	1.602
6.080	0.204	5.957	1.778
6.059	0.380	5.946	2.000
6.032	0.602	5.936	2.225
6.013	0.778	5.930	2.380
5.999	1.000	5.923	2.611
5.993	1.204	5.916	2.795
5.982	1.398	5.905	3.009
		5.896	3.193

RUN 166 MATERIAL SBR

TEMPERATURE: -6.9 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.926672

log G(t)	log t	log G(t)	log t
6.292	0.000	6.014	1.602
6.246	0.204	5.998	1.778
6.191	0.380	5.988	2.000
6.152	0.602	5.979	2.225
6.124	0.778	5.968	2.380
6.087	1.000	5.953	2.611
6.062	1.204	5.943	2.795
6.039	1.398	5.932	3.009
		5.925	3.193

RUN 188 MATERIAL SBR

TEMPERATURE: -15.9 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.895072

log G(t)	log t	log G(t)	log t
8.932	0.000	8.880	1.602
8.929	0.204	8.869	1.778
8.921	0.380	8.850	2.000
8.918	0.602	8.833	2.201
8.918	0.778	8.817	2.401
8.907	1.000	8.789	2.600
8.902	1.204	8.743	2.800
8.899	1.398	8.692	3.003

RUN 122 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.933894

log G(t)	log t	log G(t)	log t
6.026	0.000	5.950	1.602
6.021	0.176	5.943	1.778
6.009	0.398	5.934	2.000
5.995	0.602	5.922	2.225
5.985	0.778	5.915	2.380
5.973	1.000	5.905	2.611
5.964	1.204	5.895	2.820
5.956	1.398	5.887	3.009

RUN 190 MATERIAL SBR

TEMPERATURE: -8.4 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.899438

log G(t)	log t	log G(t)	log t
8.754	0.000	8.377	1.398
8.705	0.204	8.297	1.602
8.658	0.380	8.218	1.778
8.609	0.602	8.084	2.000
8.566	0.778	7.966	2.201
8.499	1.000	7.838	2.401
8.434	1.204	7.696	2.600
		7.571	2.800

RUN 189 MATERIAL SBR

TEMPERATURE: -12.3 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.897173

log G(t)	log t	log G(t)	log t
8.868	0.000	8.623	1.602
8.857	0.204	8.584	1.778
8.836	0.380	8.527	2.000
8.827	0.602	8.475	2.201
8.808	0.778	8.404	2.401
8.773	1.000	8.349	2.600
8.721	1.204	8.272	2.800
8.680	1.398	8.169	3.003

RUN 191 MATERIAL SBR

TEMPERATURE: -3.3 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.902439

log G(t)	log t	log G(t)	log t
8.393	0.000	7.493	1.602
8.316	0.204	7.367	1.806
8.239	0.380	7.242	2.000
8.128	0.602	7.109	2.204
8.030	0.778	6.981	2.408
7.889	1.000	6.859	2.602
7.747	1.204	6.741	2.798
7.619	1.398	6.620	3.000
		6.507	3.200

RUN 149 MATERIAL SBR

TEMPERATURE: -6.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.900850

log G(t)	log t	log G(t)	log t
8.425	0.778	7.836	2.000
8.354	1.000	7.696	2.204
8.274	1.204	7.562	2.408
8.187	1.398	7.444	2.602
8.082	1.602	7.322	2.798
7.964	1.806	7.190	3.000
		7.061	3.200

RUN 128 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.907326

log G(t)	log t	log G(t)	log t
7.063	0.000	6.278	1.602
6.931	0.204	6.223	1.778
6.812	0.380	6.187	2.000
6.656	0.602	6.148	2.225
6.565	0.778	6.121	2.380
6.463	1.000	6.092	2.611
6.383	1.204	6.071	2.795
6.330	1.398	6.043	3.009
		6.029	3.193

RUN 157 MATERIAL SBR

TEMPERATURE: 0.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.904367

log G(t)	log t	log G(t)	log t
7.838	0.000	6.809	1.602
7.697	0.204	6.670	1.806
7.582	0.380	6.561	2.000
7.446	0.602	6.461	2.204
7.337	0.778	6.378	2.408
7.193	1.000	6.327	2.602
7.061	1.204	6.280	2.798
6.940	1.398	6.218	3.000
		6.181	3.200

RUN 148 MATERIAL SBR

TEMPERATURE: 10.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.910279

log G(t)	log t	log G(t)	log t
6.434	0.000	6.092	1.602
6.367	0.204	6.068	1.806
6.319	0.380	6.045	2.000
6.264	0.602	6.029	2.204
6.214	0.778	6.023	2.408
6.182	1.000	6.014	2.602
6.145	1.204	5.999	2.798
6.117	1.398	5.987	3.000
		5.976	3.200

RUN 156 MATERIAL SBR

TEMPERATURE: 7.5 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.908794

log G(t)	log t	log G(t)	log t
6.684	0.000	6.161	1.602
6.588	0.204	6.125	1.806
6.488	0.380	6.101	2.000
6.392	0.602	6.076	2.204
6.346	0.778	6.051	2.408
6.292	1.000	6.032	2.602
6.228	1.204	6.022	2.798
6.190	1.398	6.016	3.000
		6.003	3.200

RUN 154 MATERIAL SBR

TEMPERATURE: 20.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.916215

log G(t)	log t	log G(t)	log t
6.103	0.000	5.987	1.602
6.079	0.204	5.978	1.806
6.056	0.380	5.971	2.000
6.041	0.602	5.964	2.204
6.035	0.778	5.957	2.408
6.025	1.000	5.948	2.602
6.010	1.204	5.937	2.798
5.998	1.398	5.929	3.000
		5.920	3.200

RUN 151 MATERIAL SBR

TEMPERATURE: 12.5 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.911752

log G(t)	log t	log G(t)	log t
6.304	0.000	6.036	1.602
6.243	0.204	6.024	1.806
6.200	0.380	6.018	2.000
6.171	0.602	6.007	2.204
6.138	0.778	5.992	2.408
6.107	1.000	5.981	2.602
6.082	1.204	5.970	2.798
6.059	1.398	5.962	3.000
		5.954	3.200

RUN 196 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 480.5 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.887547

log G(t)	log t	log G(t)	log t
8.858	0.000	8.583	1.398
8.839	0.204	8.531	1.602
8.815	0.380	8.471	1.778
8.788	0.602	8.400	2.000
8.741	0.778	8.329	2.201
8.684	1.000	8.249	2.401
8.651	1.204	8.137	2.600
		8.020	2.800

RUN 195 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 500.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.885169

log G(t)	log t	log G(t)	log t
8.872	0.000	8.703	1.398
8.869	0.204	8.637	1.602
8.864	0.380	8.596	1.778
8.842	0.602	8.528	2.000
8.823	0.778	8.465	2.201
8.796	1.000	8.411	2.401
8.746	1.204	8.334	2.600
		8.254	2.800

RUN 137 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 440.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.892740

log G(t)	log t	log G(t)	log t
8.598	0.000	8.083	1.398
8.554	0.204	7.958	1.602
8.502	0.380	7.848	1.778
8.425	0.602	7.695	2.000
8.373	0.778	7.562	2.201
8.289	1.000	7.441	2.401
8.198	1.204	7.316	2.600
		7.184	2.800

RUN 138 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 460.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.890131

log G(t)	log t	log G(t)	log t
8.741	0.000	8.287	1.602
8.695	0.204	8.200	1.778
8.648	0.380	8.074	2.000
8.607	0.602	7.957	2.201
8.563	0.778	7.822	2.401
8.495	1.000	7.686	2.600
8.430	1.204	7.560	2.800
8.366	1.398	7.437	3.003

RUN 135 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 400.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.898244

log G(t)	log t	log G(t)	log t
8.223	0.000	7.231	1.602
8.095	0.204	7.113	1.778
8.009	0.380	6.986	2.000
7.872	0.602	6.838	2.225
7.764	0.778	6.728	2.380
7.609	1.000	6.585	2.611
7.470	1.204	6.499	2.795
7.348	1.398	6.410	3.009
		6.355	3.193

RUN 136 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 420.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.895442

log G(t)	log t	log G(t)	log t
8.472	0.000	7.664	1.602
8.412	0.204	7.560	1.778
8.352	0.380	7.418	2.000
8.273	0.602	7.273	2.225
8.178	0.778	7.172	2.380
8.049	1.000	7.033	2.611
7.937	1.204	6.911	2.795
7.800	1.398	6.762	3.009

RUN 310 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 360.0 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.904177

log G(t)	log t	log G(t)	log t
7.418	0.000	6.475	1.602
7.295	0.204	6.393	1.806
7.183	0.380	6.342	2.000
7.044	0.602	6.272	2.204
6.935	0.778	6.227	2.408
6.785	1.000	6.196	2.602
6.645	1.204	6.162	2.798
6.544	1.398	6.129	3.000
		6.105	3.200

RUN 134 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 380.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.901153

log G(t)	log t	log G(t)	log t
7.855	0.000	6.943	1.398
7.708	0.204	6.819	1.602
7.593	0.380	6.702	1.778
7.454	0.602	6.586	2.000
7.336	0.778	6.484	2.225
7.202	1.000	6.424	2.380
7.062	1.204	6.360	2.611
		6.313	2.795

RUN 114 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 320.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.910609

log G(t)	log t	log G(t)	log t
6.683	0.000	6.158	1.602
6.579	0.204	6.126	1.778
6.489	0.380	6.098	2.000
6.397	0.602	6.071	2.225
6.345	0.778	6.052	2.380
6.291	1.000	6.028	2.611
6.227	1.204	6.018	2.795
6.192	1.398	6.010	3.009
		5.998	3.193

RUN 128 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.907326

log G(t)	log t	log G(t)	log t
7.063	0.000	6.278	1.602
6.931	0.204	6.223	1.778
6.812	0.380	6.187	2.000
6.656	0.602	6.148	2.225
6.565	0.778	6.121	2.380
6.463	1.000	6.092	2.611
6.383	1.204	6.071	2.795
6.330	1.398	6.043	3.009
		6.029	3.193

RUN 124 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 280.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.917626

log G(t)	log t	log G(t)	log t
6.287	0.000	6.025	1.602
6.231	0.176	6.015	1.778
6.188	0.398	6.007	2.000
6.155	0.602	5.993	2.225
6.123	0.778	5.983	2.380
6.094	1.000	5.969	2.611
6.070	1.204	5.959	2.820
6.046	1.398	5.951	3.009

RUN 126 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 300.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.914038

log G(t)	log t	log G(t)	log t
6.429	0.000	6.075	1.602
6.354	0.204	6.054	1.778
6.311	0.380	6.027	2.000
6.248	0.602	6.010	2.225
6.199	0.778	6.005	2.380
6.166	1.000	5.993	2.611
6.128	1.204	5.981	2.795
6.098	1.398	5.967	3.009
		5.958	3.193

RUN 122 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.933894

log G(t)	log t	log G(t)	log t
6.026	0.000	5.950	1.602
6.021	0.176	5.943	1.778
6.009	0.398	5.934	2.000
5.995	0.602	5.922	2.225
5.985	0.778	5.915	2.380
5.973	1.000	5.905	2.611
5.964	1.204	5.895	2.820
5.956	1.398	5.887	3.009

RUN 123 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 240.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.925339

log G(t)	log t	log G(t)	log t
6.100	0.000	5.972	1.602
6.080	0.176	5.962	1.778
6.053	0.398	5.952	2.000
6.029	0.602	5.944	2.225
6.015	0.778	5.939	2.380
6.008	1.000	5.931	2.611
5.996	1.204	5.921	2.820
5.984	1.398	5.911	3.009

RUN 119 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 80.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.966993

log G(t)	log t	log G(t)	log t
5.896	0.000	5.837	1.602
5.888	0.176	5.830	1.778
5.878	0.398	5.823	2.000
5.869	0.602	5.816	2.225
5.861	0.778	5.812	2.380
5.852	1.000	5.805	2.611
5.847	1.204	5.800	2.820
5.843	1.398	5.795	3.009

RUN 121 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 160.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 0.943487

log G(t)	log t	log G(t)	log t
5.974	0.000	5.905	1.602
5.965	0.176	5.897	1.778
5.954	0.398	5.886	2.000
5.946	0.602	5.876	2.225
5.940	0.778	5.871	2.380
5.933	1.000	5.865	2.611
5.923	1.204	5.860	2.820
5.914	1.398	5.854	3.009

RUN 117 MATERIAL SBR

TEMPERATURE: 5.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 1.270 CM
LENGTH: 6.731 CM

V/V(TO,PO) = 1.00000

log G(t)	log t	log G(t)	log t
5.835	0.000	5.788	1.602
5.831	0.204	5.784	1.778
5.826	0.380	5.779	2.000
5.818	0.602	5.774	2.201
5.813	0.778	5.770	2.401
5.807	1.000	5.765	2.600
5.800	1.204	5.763	2.800
5.794	1.398	5.758	3.003

RUN 240 MATERIAL BR

TEMPERATURE: -60.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.953009

log G(t)	log t	log G(t)	log t
8.694	0.000	8.648	1.398
8.690	0.204	8.612	1.602
8.689	0.380	8.570	1.806
8.688	0.602	8.515	2.000
8.685	0.778	8.448	2.204
8.676	1.000	8.370	2.408
8.665	1.204	8.272	2.602

RUN 242 MATERIAL BR

TEMPERATURE: -52.5 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.958323

log G(t)	log t	log G(t)	log t
8.629	0.000	7.995	1.602
8.590	0.204	7.866	1.806
8.551	0.380	7.726	2.000
8.484	0.602	7.572	2.204
8.424	0.778	7.421	2.408
8.334	1.000	7.282	2.602
8.222	1.204	7.141	2.798
8.115	1.398	6.989	3.000
		6.850	3.200

RUN 243 MATERIAL BR

TEMPERATURE: -56.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.955837

log G(t)	log t	log G(t)	log t
8.680	0.000	8.381	1.398
8.669	0.204	8.281	1.602
8.655	0.380	8.166	1.806
8.617	0.602	8.056	2.000
8.583	0.778	7.930	2.204
8.522	1.000	7.791	2.408
8.455	1.204	7.646	2.602
		7.499	2.798

RUN 239 MATERIAL BR

TEMPERATURE: -47.9 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.961587

log G(t)	log t	log G(t)	log t
8.432	0.204	7.421	1.806
8.356	0.380	7.283	2.000
8.231	0.602	7.135	2.204
8.134	0.778	6.983	2.408
8.002	1.000	6.851	2.602
7.869	1.204	6.741	2.798
7.726	1.398	6.648	3.000
7.572	1.602	6.566	3.200

RUN 238 MATERIAL BR

TEMPERATURE: -50.3 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.959905

log G(t)	log t	log G(t)	log t
8.626	0.000	7.923	1.602
8.583	0.204	7.780	1.806
8.532	0.380	7.633	2.000
8.458	0.602	7.481	2.204
8.390	0.778	7.334	2.408
8.275	1.000	7.194	2.602
8.161	1.204	7.048	2.798
8.049	1.398	6.904	3.000
		6.781	3.200

RUN 235 MATERIAL BR

TEMPERATURE: -40.6 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.966808

log G(t)	log t	log G(t)	log t
7.848	0.000	6.724	1.602
7.696	0.204	6.632	1.806
7.563	0.380	6.555	2.000
7.400	0.602	6.483	2.204
7.275	0.778	6.419	2.408
7.112	1.000	6.366	2.602
6.961	1.204	6.317	2.798
6.834	1.398	6.269	3.000

RUN 236 MATERIAL BR

TEMPERATURE: -43.6 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.2577 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.964651

log G(t)	log t	log G(t)	log t
8.117	0.000	6.988	1.602
7.996	0.204	6.847	1.806
7.884	0.380	6.734	2.000
7.724	0.602	6.637	2.204
7.591	0.778	6.553	2.408
7.426	1.000	6.482	2.602
7.280	1.204	6.417	2.798
7.139	1.398	6.360	3.000
		6.308	3.200

RUN 213 MATERIAL BR

TEMPERATURE: -29.7 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.974656

log G(t)	log t	log G(t)	log t
6.827	0.000	6.277	1.602
6.721	0.204	6.236	1.806
6.644	0.380	6.204	2.000
6.557	0.602	6.177	2.204
6.495	0.778	6.153	2.408
6.427	1.000	6.131	2.602
6.372	1.204	6.112	2.798
6.324	1.398	6.094	3.000
		6.079	3.200

RUN 216 MATERIAL BR

TEMPERATURE: -35.1 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.970737

log G(t)	log t	log G(t)	log t
7.253	0.000	6.411	1.602
7.104	0.204	6.355	1.806
6.973	0.380	6.306	2.000
6.825	0.602	6.258	2.204
6.728	0.778	6.215	2.408
6.626	1.000	6.182	2.602
6.546	1.204	6.154	2.798
6.476	1.398	6.130	3.000
		6.107	3.200

RUN 211 MATERIAL BR

TEMPERATURE: -10.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.988940

log G(t)	log t	log G(t)	log t
6.290	0.000	6.098	1.602
6.251	0.204	6.085	1.806
6.222	0.380	6.076	2.000
6.193	0.602	6.068	2.204
6.173	0.778	6.057	2.408
6.149	1.000	6.046	2.602
6.130	1.204	6.034	2.798
6.112	1.398	6.021	3.000
		6.009	3.200

RUN 212 MATERIAL BR

TEMPERATURE: -20.5 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.981307

log G(t)	log t	log G(t)	log t
6.451	0.000	6.135	1.602
6.393	0.204	6.113	1.806
6.348	0.380	6.095	2.000
6.294	0.602	6.078	2.204
6.255	0.778	6.064	2.408
6.214	1.000	6.053	2.602
6.183	1.204	6.044	2.798
6.157	1.398	6.034	3.000
		6.024	3.200

RUN 281 MATERIAL BR

TEMPERATURE: -20.8 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.916262

log G(t)	log t	log G(t)	log t
8.822	0.000	8.279	1.602
8.785	0.204	8.166	1.806
8.759	0.380	8.050	2.000
8.705	0.602	7.919	2.204
8.641	0.778	7.769	2.408
8.568	1.000	7.622	2.602
8.486	1.204	7.478	2.798
8.393	1.398	7.333	3.000
		7.187	3.200

RUN 209 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 1.00000

log G(t)	log t	log G(t)	log t
6.167	0.000	6.057	1.602
6.146	0.204	6.045	1.806
6.129	0.380	6.033	2.000
6.111	0.602	6.020	2.204
6.099	0.778	6.008	2.408
6.086	1.000	6.000	2.602
6.076	1.204	5.995	2.798
6.067	1.398	5.994	3.000
		5.993	3.200

RUN 276 MATERIAL BR

TEMPERATURE: -15.1 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.920098

log G(t)	log t	log G(t)	log t
8.713	0.000	7.928	1.602
8.640	0.204	7.778	1.806
8.583	0.380	7.632	2.000
8.494	0.602	7.480	2.204
8.411	0.778	7.334	2.408
8.288	1.000	7.193	2.602
8.175	1.204	7.047	2.798
8.059	1.398	6.910	3.000
		6.796	3.200

RUN 280 MATERIAL BR

TEMPERATURE: -17.7 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.918336

log G(t)	log t	log G(t)	log t
8.762	0.000	8.059	1.602
8.712	0.204	7.928	1.806
8.647	0.380	7.786	2.000
8.575	0.602	7.633	2.204
8.505	0.778	7.481	2.408
8.401	1.000	7.342	2.602
8.288	1.204	7.201	2.798
8.180	1.398	7.050	3.000
		6.911	3.200

RUN 274 MATERIAL BR

TEMPERATURE: -9.7 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.923748

log G(t)	log t	log G(t)	log t
8.346	0.000	7.267	1.602
8.233	0.204	7.116	1.806
8.132	0.380	6.975	2.000
7.995	0.602	6.849	2.204
7.873	0.778	6.746	2.408
7.707	1.000	6.663	2.602
7.554	1.204	6.587	2.798
7.413	1.398	6.517	3.000
		6.456	3.200

RUN 275 MATERIAL BR

TEMPERATURE: -13.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.921527

log G(t)	log t	log G(t)	log t
8.611	0.000	7.677	1.602
8.530	0.204	7.525	1.806
8.450	0.380	7.386	2.000
8.328	0.602	7.238	2.204
8.230	0.778	7.086	2.408
8.100	1.000	6.951	2.602
7.971	1.204	6.836	2.798
7.831	1.398	6.739	3.000
		6.656	3.200

RUN 270 MATERIAL BR

TEMPERATURE: -3.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.928311

log G(t)	log t	log G(t)	log t
7.711	0.000	6.650	1.602
7.558	0.204	6.569	1.806
7.429	0.380	6.501	2.000
7.270	0.602	6.437	2.204
7.141	0.778	6.381	2.408
6.978	1.000	6.334	2.602
6.845	1.204	6.289	2.798
6.741	1.398	6.247	3.000
		6.212	3.200

RUN 273 MATERIAL BR

TEMPERATURE: -6.5 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.925925

log G(t)	log t	log G(t)	log t
8.065	0.000	6.916	1.602
7.934	0.204	6.797	1.806
7.807	0.380	6.706	2.000
7.640	0.602	6.622	2.204
7.509	0.778	6.546	2.408
7.350	1.000	6.481	2.602
7.202	1.204	6.426	2.798
7.057	1.398	6.373	3.000
		6.327	3.200

RUN 247 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.933782

log G(t)	log t	log G(t)	log t
7.101	0.000	6.410	1.602
6.958	0.204	6.360	1.806
6.853	0.380	6.317	2.000
6.744	0.602	6.279	2.204
6.670	0.778	6.247	2.408
6.587	1.000	6.223	2.602
6.519	1.204	6.201	2.798
6.462	1.398	6.179	3.000
		6.160	3.200

RUN 269 MATERIAL BR

TEMPERATURE: 0.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.930364

log G(t)	log t	log G(t)	log t
7.504	0.000	6.567	1.602
7.358	0.204	6.500	1.806
7.230	0.380	6.445	2.000
7.065	0.602	6.394	2.204
6.944	0.778	6.345	2.408
6.815	1.000	6.303	2.602
6.720	1.204	6.268	2.798
6.641	1.398	6.237	3.000
		6.212	3.200

RUN 297 MATERIAL BR

TEMPERATURE: -2.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.903140

log G(t)	log t	log G(t)	log t
8.938	0.000	8.456	1.602
8.904	0.204	8.344	1.806
8.872	0.380	8.237	2.000
8.819	0.602	8.118	2.204
8.764	0.778	7.989	2.408
8.699	1.000	7.850	2.602
8.623	1.204	7.702	2.798
8.549	1.398	7.552	3.000
		7.408	3.200

RUN 299 MATERIAL BR

TEMPERATURE: 10.0 DEG C
PRESSURE: 200.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.937213

log G(t)	log t	log G(t)	log t
6.802	0.000	6.306	1.602
6.711	0.204	6.270	1.806
6.641	0.380	6.243	2.000
6.562	0.602	6.219	2.204
6.505	0.778	6.196	2.408
6.445	1.000	6.176	2.602
6.394	1.204	6.158	2.798
6.348	1.398	6.142	3.000
		6.129	3.200

RUN 294 MATERIAL BR

TEMPERATURE: 3.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.906453

log G(t)	log t	log G(t)	log t
8.784	0.000	8.048	1.602
8.727	0.204	7.910	1.806
8.667	0.380	7.765	2.000
8.583	0.602	7.612	2.204
8.509	0.778	7.462	2.408
8.397	1.000	7.324	2.602
8.282	1.204	7.179	2.798
8.173	1.398	7.032	3.000
		6.902	3.200

RUN 296 MATERIAL BR

TEMPERATURE: 0.6 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.904868

log G(t)	log t	log G(t)	log t
8.867	0.000	8.231	1.602
8.816	0.204	8.111	1.806
8.761	0.380	7.988	2.000
8.696	0.602	7.842	2.204
8.630	0.778	7.688	2.408
8.545	1.000	7.544	2.602
8.450	1.204	7.403	2.798
8.344	1.398	7.257	3.000
		7.109	3.200

RUN 292 MATERIAL BR

TEMPERATURE: 7.7 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.909579

log G(t)	log t	log G(t)	log t
8.309	0.380	7.335	1.806
8.184	0.602	7.193	2.000
8.077	0.778	7.043	2.204
7.929	1.000	6.910	2.408
7.776	1.204	6.807	2.602
7.630	1.398	6.720	2.798
7.481	1.602	6.640	3.000
		6.569	3.200

RUN 259 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.907790

log G(t)	log t	log G(t)	log t
8.699	0.000	7.963	1.398
8.623	0.204	7.811	1.602
8.550	0.380	7.658	1.806
8.439	0.602	7.515	2.000
8.341	0.778	7.369	2.204
8.216	1.000	7.220	2.408
8.093	1.204	7.077	2.602
		6.948	2.798

RUN 291 MATERIAL BR

TEMPERATURE: 13.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.913130

log G(t)	log t	log G(t)	log t
8.072	0.000	6.923	1.602
7.937	0.204	6.813	1.806
7.806	0.380	6.726	2.000
7.638	0.602	6.646	2.204
7.509	0.778	6.573	2.408
7.351	1.000	6.512	2.602
7.201	1.204	6.459	2.798
7.058	1.398	6.408	3.000

RUN 290 MATERIAL BR

TEMPERATURE: 10.1 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.911187

log G(t)	log t	log G(t)	log t
8.315	0.000	7.364	1.398
8.201	0.204	7.214	1.602
8.095	0.380	7.063	1.806
7.950	0.602	6.934	2.000
7.820	0.778	6.821	2.204
7.652	1.000	6.729	2.408
7.502	1.204	6.651	2.602
		6.581	2.798

RUN 288 MATERIAL BR

TEMPERATURE: 19.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.917148

log G(t)	log t	log G(t)	log t
7.517	0.000	6.591	1.602
7.371	0.204	6.526	1.806
7.243	0.380	6.473	2.000
7.078	0.602	6.421	2.204
6.960	0.778	6.373	2.408
6.836	1.000	6.333	2.602
6.743	1.204	6.298	2.798
6.665	1.398	6.269	3.000
		6.244	3.200

RUN 289 MATERIAL BR

TEMPERATURE: 16.2 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.915263

log G(t)	log t	log G(t)	log t
7.802	0.000	6.744	1.602
7.649	0.204	6.665	1.806
7.520	0.380	6.597	2.000
7.362	0.602	6.533	2.204
7.232	0.778	6.478	2.408
7.069	1.000	6.430	2.602
6.937	1.204	6.383	2.798
6.834	1.398	6.343	3.000
		6.309	3.200

RUN 286 MATERIAL BR

TEMPERATURE: 25.1 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.921265

log G(t)	log t	log G(t)	log t
7.041	0.000	6.424	1.602
6.915	0.204	6.377	1.806
6.826	0.380	6.340	2.000
6.730	0.602	6.307	2.204
6.663	0.778	6.280	2.408
6.587	1.000	6.258	2.602
6.525	1.204	6.237	2.798
6.475	1.398	6.217	3.000
		6.199	3.200

RUN 287 MATERIAL BR

TEMPERATURE: 21.9 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.919104

log G(t)	log t	log G(t)	log t
7.275	0.000	6.491	1.602
7.124	0.204	6.439	1.806
7.000	0.380	6.392	2.000
6.868	0.602	6.347	2.204
6.783	0.778	6.309	2.408
6.691	1.000	6.279	2.602
6.614	1.204	6.254	2.798
6.550	1.398	6.232	3.000
		6.211	3.200

RUN 268 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 460.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.891083

log G(t)	log t	log G(t)	log t
8.990	0.000	8.706	1.602
8.981	0.204	8.630	1.806
8.974	0.380	8.555	2.000
8.949	0.602	8.459	2.204
8.919	0.778	8.346	2.408
8.879	1.000	8.239	2.602
8.826	1.204	8.124	2.798
8.768	1.398	7.995	3.000
		7.852	3.200

RUN 284 MATERIAL BR

TEMPERATURE: 29.3 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.924105

log G(t)	log t	log G(t)	log t
6.791	0.000	6.323	1.602
6.705	0.204	6.291	1.806
6.639	0.380	6.265	2.000
6.564	0.602	6.243	2.204
6.512	0.778	6.221	2.408
6.454	1.000	6.202	2.602
6.404	1.204	6.185	2.798
6.361	1.398	6.171	3.000
		6.159	3.200

RUN 264 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 420.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.896235

log G(t)	log t	log G(t)	log t
8.901	0.000	8.310	1.602
8.860	0.204	8.195	1.806
8.809	0.380	8.078	2.000
8.746	0.602	7.942	2.204
8.687	0.778	7.791	2.408
8.604	1.000	7.644	2.602
8.521	1.204	7.501	2.798
8.424	1.398	7.356	3.000
		7.210	3.200

RUN 266 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 440.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.893613

log G(t)	log t	log G(t)	log t
8.974	0.000	8.506	1.602
8.941	0.204	8.397	1.806
8.910	0.380	8.290	2.000
8.861	0.602	8.172	2.204
8.804	0.778	8.046	2.408
8.743	1.000	7.910	2.602
8.668	1.204	7.763	2.798
8.596	1.398	7.611	3.000
		7.467	3.200

RUN 262 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 380.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.901783

log G(t)	log t	log G(t)	log t
8.815	0.000	8.118	1.602
8.752	0.204	7.990	1.806
8.702	0.380	7.852	2.000
8.621	0.602	7.698	2.204
8.554	0.778	7.546	2.408
8.455	1.000	7.406	2.602
8.344	1.204	7.265	2.798
8.237	1.398	7.116	3.000
		6.972	3.200

RUN 263 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 400.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.898956

log G(t)	log t	log G(t)	log t
8.890	0.000	8.280	1.602
8.846	0.204	8.164	1.806
8.791	0.380	8.044	2.000
8.729	0.602	7.905	2.204
8.667	0.778	7.751	2.408
8.584	1.000	7.606	2.602
8.495	1.204	7.463	2.798
8.394	1.398	7.318	3.000
		7.171	3.200

RUN 259 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 340.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.907790

log G(t)	log t	log G(t)	log t
8.699	0.000	7.963	1.398
8.623	0.204	7.811	1.602
8.550	0.380	7.658	1.806
8.439	0.602	7.515	2.000
8.341	0.778	7.369	2.204
8.216	1.000	7.220	2.408
8.093	1.204	7.077	2.602
		6.948	2.798

RUN 261 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 360.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.904725

log G(t)	log t	log G(t)	log t
8.780	0.000	8.034	1.602
8.722	0.204	7.892	1.806
8.660	0.380	7.747	2.000
8.576	0.602	7.594	2.204
8.501	0.778	7.446	2.408
8.385	1.000	7.307	2.602
8.271	1.204	7.163	2.798
8.161	1.398	7.016	3.000

RUN 254 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 300.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.914334

log G(t)	log t	log G(t)	log t
8.324	0.000	7.224	1.602
8.210	0.204	7.073	1.806
8.104	0.380	6.943	2.000
7.959	0.602	6.830	2.204
7.829	0.778	6.738	2.408
7.662	1.000	6.661	2.602
7.511	1.204	6.590	2.798
7.373	1.398	6.525	3.000
		6.471	3.200

RUN 255 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 320.0 MPa

ANGLE: 0.1433 RADIANS

DIAMETER: 0.317 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.910989

log G(t)	log t	log G(t)	log t
8.401	0.204	7.330	1.806
8.303	0.380	7.187	2.000
8.178	0.602	7.037	2.204
8.071	0.778	6.904	2.408
7.923	1.000	6.801	2.602
7.771	1.204	6.714	2.798
7.625	1.398	6.635	3.000
7.475	1.602	6.564	3.200

RUN 251 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 240.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.925385

log G(t)	log t	log G(t)	log t
7.592	0.000	6.621	1.602
7.444	0.204	6.550	1.806
7.318	0.380	6.492	2.000
7.154	0.602	6.438	2.204
7.025	0.778	6.388	2.408
6.885	1.000	6.343	2.602
6.782	1.204	6.305	2.798
6.698	1.398	6.272	3.000
		6.245	3.200

RUN 250 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 120.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.954029

log G(t)	log t	log G(t)	log t
6.495	0.000	6.185	1.602
6.438	0.204	6.164	1.806
6.393	0.380	6.146	2.000
6.340	0.602	6.129	2.204
6.302	0.778	6.116	2.408
6.262	1.000	6.105	2.602
6.232	1.204	6.096	2.798
6.208	1.398	6.086	3.000
		6.076	3.200

RUN 209 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 0.1 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 1.00000

log G(t)	log t	log G(t)	log t
6.167	0.000	6.057	1.602
6.146	0.204	6.045	1.806
6.129	0.380	6.033	2.000
6.111	0.602	6.020	2.204
6.099	0.778	6.008	2.408
6.086	1.000	6.000	2.602
6.076	1.204	5.995	2.798
6.067	1.398	5.994	3.000
		5.993	3.200

RUN 244 MATERIAL BR

TEMPERATURE: 5.0 DEG C
PRESSURE: 40.0 MPa

ANGLE: 0.0349 RADIANS

DIAMETER: 0.952 CM
LENGTH: 6.858 CM

V/V(TO,PO) = 0.981567

log G(t)	log t	log G(t)	log t
6.247	0.000	6.091	1.602
6.217	0.204	6.083	1.806
6.196	0.380	6.073	2.000
6.172	0.602	6.063	2.204
6.153	0.778	6.050	2.408
6.132	1.000	6.038	2.602
6.116	1.204	6.026	2.798
6.103	1.398	6.015	3.000
		6.006	3.200