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I am submitting herewith a thesis written by Bradley D. Snow entitled "A Unified Model for the Rubbery and Glassy States: Volume Aging and Orientation Aging in Polystyrene." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

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A UNIFIED MODEL FOR THE RUBBERY AND GLASSY STATES: VOLUME AGING AND ORIENTATION AGING IN POLYSTYRENE

A Thesis

Presented for the

Master of Science

Degree

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ABSTRACT

When a molten polymer is quenched from the rubbery state to the glassy state, nonequilibrium properties are frozen into the material. Two such properties of considerable interest in characterizing the behavior of the glassy state are the so-called "free volume" and the molecular orientation. Both of these properties were considered in this thesis. A major objective of the work was to develop a unified theoretical approach to connect the two states. Such a unified treatment provides the means through which the glassy state is directly related to the thermal and deformation history experienced in the rubbery state.

The time dependent volume behavior of polystyrene was investigated at 90°C, 70°C, and 25°C. Nonequilibrium free volume was frozen into the samples by quenching them in ice water from about 120°C. The decay of the free volume was then monitored at the above three temperatures. At 90°C and 70°C there was an initial period (100 hours or less) of rapid aging after which the change in free volume was very slow. At 25°C the aging was considerably slower.

An explicit form has been suggested for a general viscoelastic model including compressible effects. When the appropriate restrictions are imposed the model reduces to either incompressible viscoelasticity or to classical linear elasticity. Also, under certain circumstances, the general model reduces to a volume rate equation. The rate equation was used to fit the volume data described above,

and also to predict the effect of the cooling rate on the glass transition temperature.

The incompressible form of the general model was used to analyze orientation aging data obtained by Potnis. The analysis involved following the history of the sample including the deformation in the rubbery state and cooling to the glassy state. The orientation, induced through the deformation and frozen into the glass, slowly decays with a corresponding shrinkage of the sample. The effect of an external load on the shrinkage was also considered. The analysis was shown to be capable of providing a good fit of the experimental shrinkage data.

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CHAPTER I

INTRODUCTION

Polymer products are usually fabricated through some kind of nonisothermal process, involving shaping or molding the material as a melt, followed by a temperature decrease to obtain the solid form. A procedure of this type may freeze into the final product nonequilibrium properties which persist from the prior rubbery state. Two such properties are "free volume" and molecular orientation. Free volume will be discussed in detail in Chapter II, but, for the present, will simply be described as that part of the volume which is available for molecular rearrangement. Nonequilibrium free volume, and its decay with time, referred to as physical aging, have been extensively studied. The free volume has a direct effect on the mechanical properties of the polymer and therefore physical aging is of practical as well as theoretical importance. Molecular orientation will also be frozen into the solid if the polymer is being deformed during the quench. This orientation may enhance the mechanical properties of the material; however, it too will deteriorate with time, quite rapidly if the temperature is brought near the glass transition temperature, T_g. The nonisothermal nature of the processing operations also affects the level of T_g, and, since many polymer properties change during the glass transition, the cooling rate dependence of it is of considerable interest.

A theoretical treatment of quenching from the rubbery state to the glassy state will obviously involve rheological equations for both states. The theories used in these two states are quite different; at temperatures above T_g a viscoelastic model is used to describe the polymer stress-strain behavior, while at lower temperatures, the equations are usually of a linearly elastic nature. Since temperature ranges of interest typically include T_g, it would be most useful to have a single model applicable both above and below T_g. However, several conceptual difficulties are encountered. First, viscoelasticity, at least as it is actually applied, is limited to incompressible materials. Since a variation in the thermal coefficient of expansion is one of the notable changes that occurs at T_g, a model which is applicable during the glass transition should include compressible effects. Moreover, even at constant temperature, one of the characteristic features of the glassy state is the volume change accompanying deformation. While classical linear elasticity is not restricted to incompressible materials, it is, like all theories of elasticity, an equilibrium theory. Consequently, if one wishes to describe time dependent aging behavior of amorphous glasses an elastic model is clearly inadequate; for such purposes a rate equation may be employed, however, it is independent of the elastic constitutive equation. Volume aging has been extensively modeled with such a rate equation and will be described in detail in Chapter II.

At The University of Tennessee, considerable effort has gone into the use of nonisothermal viscoelastic equations to model various deformations in the presence of cooling at temperatures above T_g. However, if the temperature range of the problem spans T_g, difficulties have been encountered. Recent studies at The University of Tennessee have included a project to quantify the effect of the cooling rate on T_g. Also investigated was the effect of the cooling rate on the amount of free volume present at the end of the quench, followed by free volume aging at room temperature. A separate project addressed the question of orientation aging at three temperatures somewhat less than T_g.

The present research is a continuation of these efforts. Free volume aging following a fast quench was studied at room temperature, 70°C, and 90°C, and the experimental data were fit with a rate equation. An explicit form has been suggested for a viscoelastic constitutive equation, such that the rate equation may be derived from it as a special case. The constitutive equation was also used to correlate the set of previously mentioned orientation aging data. This required tracing the polymer history from the rubbery state, through the deformation, down into the glassy state. In particular, the temperature dependence of both the relaxation time and the modulus was considered.

CHAPTER II

BACKGROUND

The literature which is pertinent to the research presented later in this thesis will first be reviewed. The subjects of elasticity and viscoelasticity are considered, followed by a discussion of the glass transition temperature, the rubbery state, and the glassy state. Finally, free volume and volume aging, and molecular orientation and orientation aging will be discussed in detail.

A. ELASTICITY AND VISCOELASTICITY

The stress-strain behavior of polymers is generally considered to be elastic or viscoelastic depending on the particular polymer and the temperature. A perfectly elastic solid may be described (1) as a material which instantly attains a unique equilibrium shape at a state of zero stress, and which, if held in any nonequilibrium shape, results in stresses that instantaneously reach a nonzero equilibrium value. If either of the above two events occur over a finite time, the substance is considered to be viscoelastic. Stress relaxation and elastic recovery are two well-known time dependent phenomena that illustrate the viscoelastic nature of polymers (2,3). Elastic recovery will be reviewed further in Chapter VI since it is the process by which orientation aging occurs.

Large Deformation (Nonlinear) Elasticity

Large deformation elasticity, also referred to as nonlinear elasticity, is used to describe the elastic behavior of materials which have undergone large deformations. A familiar example of the use of this theory is to describe the stress-strain behavior of crosslinked rubber materials subjected to large strains. The theory for such materials has evolved along two separate routes: the continuum approach and the kinetic molecular approach. They are related in that they both utilize the concept of a strain energy potential, but the former postulates that the strain energy is a function of strain invariants, while the latter employs entropic arguments to obtain an equation for the stress.

The continuum theory, essentially due to Finger (4), provides an explicit relationship between the stress and the strain energy, and, moreover, by assuming the strain energy is a function of strain invariants one is eventually led to (5,6) the following equation*

$$\sigma_{ij} = \frac{2}{III^{1/2}} \left[\left(II \frac{\partial W}{\partial II} + III \frac{\partial W}{\partial III} \right) \delta_{ij} + \frac{\partial W}{\partial I} c_{ij}^{-1} - III \frac{\partial W}{\partial II} c_{ij} \right] \qquad \text{(II-1)}$$

where σ_{ij} is the stress, W is a strain energy function, c_{ij}^{-1} and c_{ij} are the Finger and Cauchy strain tensors, I, II, and III are the three invariants of c_{ij}^{-1}, and δ_{ij} is the Kronecker delta.

---

*All equations written in component notation are restricted to Cartesian coordinates.

Equation (II-1) may also be written in other equivalent forms by utilizing relationships between the invariants of c_{ij} and c_{ij}^{-1} (6). The assumption that W is a function only of strain invariants restricts equation (II-1) to isotropic materials.

Equation (II-1) is seldom used as presented above, because rubbery materials are usually considered to be incompressible, in which case simplification of the equation is possible. The third invariant of c_{ij}^{-1} is related to volume changes by the equation

$$III^{1/2} = \frac{V}{V_o} \qquad \text{(II-2)}$$

where V is the volume and V_o is a reference volume. For incompressible media, therefore, III = 1, and W depends only on the first two invariants. The corresponding equation for the stress takes form (7,8)

$$\sigma_{ij} = -p\delta_{ij} + 2\left[\frac{\partial W}{\partial I} c_{ij}^{-1} - \frac{\partial W}{\partial II} c_{ij}\right] \qquad \text{(II-3)}$$

where p is an indeterminate scalar. Equation (II-3) is generally considered to be the starting point for problems in rubber elasticity (9). The application of equation (II-3) requires a functional form for W; Mooney (10) has shown, from stress-strain considerations, that the most general first order function is

$$W = C_1(I - 3) + C_2(II - 3) \qquad \text{(II-4)}$$

where C_1 and C_2 are constants. The kinetic theory of rubber elasticity, mentioned earlier, also provides an equation for the strain energy function (9,11), namely

$$W = \frac{1}{2} NkT(I - 3) \qquad \text{(II-5)}$$

where N is the number of polymer chains per unit volume, k is the Boltzmann constant, and T the absolute temperature. Thus, from the kinetic theory, one concludes $C_1 = \frac{1}{2} NkT$ and $C_2 = 0$. The Mooney equation generally gives better agreement with experiment than does the kinetic form, and, therefore, considerable effort has been devoted toward a molecular interpretation of the constant C_2. However, arguments to rationalize it are varied (12) and its origin can probably be traced to several sources.

Peng and Landel (13) have used equation (II-1), with III $\neq$ 1, to describe compressible rubberlike materials under large strain. Introducing new combinations of invariants, as suggested by Penn (14), they derive an equation for W in which the distortional change and volume change appear separately. They furthermore demonstrated that the volume change contribution to the total tensile stress may be separated from the distortional contribution.

Linear Elasticity

Consideration is now given to linear elasticity, a subject normally considered separately from the previous theory; however,

it is possible to derive the isotropic linear results from equation (II-1), as will be discussed. This is the type of theory applied to solids, including glassy polymers, which have undergone small, elastic deformations. Compressibility is necessarily included because such materials exhibit volume changes upon being deformed.

The equations of classical linear elasticity (15) rest on the assumption that stress and strain are related by a linear expression of the form

$$\sigma_{ij} = c_{ijkm}\tilde{\varepsilon}_{km} \qquad \text{(II-6)}$$

where c_{ijkm} is an array of elastic constants and $\tilde{\varepsilon}_{km}$ is the linear strain. Equation (II-6) is a generalized form of Hooke's law. There are 81 components of c_{ijkm}; however, due to the symmetry of the stress and strain tensors, the maximum number of distinct elastic constants is reduced to 36 (12). Equation (II-6), as written, is applicable to anisotropic media, and in this sense is more general than the equations of the prior section on large deformation elasticity. Most real materials exhibit some inherent symmetry which permits the number of independent c_{ijkm} to be reduced still further (16). Ultimately, for a completely isotropic material, the number of independent elastic constants is only two and Hooke's law takes the familiar form (16)

$$\sigma_{ij} = \lambda\tilde{\varepsilon}_{kk}\delta_{ij} + 2G\tilde{\varepsilon}_{ij} \qquad \text{(II-7)}$$

where λ and G are referred to as Lamé's constants. Equation (II-7) may be written in other equivalent forms (12) in terms of Poisson's ratio. The quantity $\tilde{\varepsilon}_{kk}$ in equation (II-7) is related to the compressibility through the relationship (12,16)

$$\tilde{\varepsilon}_{kk} = \frac{\Delta V}{V_o} \quad . \tag{II-8}$$

It is noted that equations (II-1) and (II-7) are similar in the sense that both include compressible effects and both are restricted to isotropic media. Eringen (6) has shown how equation (II-7) may be derived from (II-1) by choosing a particular strain energy function and linearizing the resulting equation. However, the function was selected so that $\frac{\partial W}{\partial III} \cong 0$, and therefore his particular choice for W is not general.

The incompressible form of equation (II-7) may be obtained in the same manner as equation (II-3) was obtained as a special case of (II-1). For an incompressible material Poisson's ratio is $\frac{1}{2}$ and $\tilde{\varepsilon}_{kk} \to 0$; these two restrictions are possible only if $\lambda \to \infty$ and thus $\lambda\tilde{\varepsilon}_{kk}$ is indeterminate. Equation (II-7) then takes the form (16)

$$\sigma_{ij} = -p\delta_{ij} + 2G\tilde{\varepsilon}_{ij} \quad . \tag{II-9}$$

Finally, the necessary modification of the foregoing linear theory to include thermal stresses is briefly considered. One difficulty in such a treatment is that the reference volume, V_o,

becomes a function of temperature. Timoshenko and Goodier (17) write equations which are equivalent to the following modified form of equation (II-7)

$$\sigma_{ij} = [\lambda\tilde{\varepsilon}_{kk} - \alpha(\frac{2}{3}G + \lambda)(T - T_o)]\delta_{ij} + 2G\tilde{\varepsilon}_{ij} \qquad \text{(II-10)}$$

where α is the thermal coefficient of expansion, T is the temperature, and T_o a reference temperature. Apparently, equation (II-10) is motivated by the requirement that the volume "track" the temperature according to the following equation

$$V = V_o - \alpha(T_o - T)V_o \qquad \text{(II-11)}$$

which is readily derived from the definition of α assuming $\alpha(T - T_o)$ is small. If there is no applied stress equation (II-10) gives

$$\sigma_{kk} = 0 = 3\lambda\tilde{\varepsilon}_{kk} - \alpha(2G + 3\lambda)(T - T_o) + 2G\tilde{\varepsilon}_{kk} \qquad \text{(II-12)}$$

which, using $\tilde{\varepsilon}_{kk} = (V - V_o)/V_o$, reduces to equation (II-11).

Viscoelasticity

Polymer melts and concentrated solutions typically exhibit viscoelastic behavior. This term is descriptive of the intermediate position of polymers between a viscous liquid and an elastic solid. A perfectly viscous liquid may be described (1) as a material which

has no unique equilibrium shape, and which, if held in a constant shape, results in stresses that instantaneously become zero. The elastic solid was defined at the beginning of this chapter. The mechanical response of polymers may be anywhere between these two extremes, depending on the temperature and the experimental time scale (12). At low temperature or high frequency a polymer may display linearly elastic behavior, characterized by a high modulus and failure at low strains. If the temperature is increased or the frequency decreased, the same polymer may reveal a much more viscous nature, including a substantially lower modulus and permanent deformation under load.

Qualitatively, this varying behavior may be rationalized through the idea of relaxation times or the concept of memory (18). At the elastic end of the spectrum the relaxation time is infinite, or, equivalently, the memory is complete. On the other hand, a completely viscous material has a relaxation time of zero and, thus, no memory. Polymers are said to have "fading memory" (18); that is, the material remembers past configurations, but those of the recent past are the most distinct. Further consideration will be given to relaxation times and memory functions later in this thesis.

The equations of viscoelasticity are of many forms and may be motivated in different ways. No attempt is made here to classify the numerous models; recent review articles by Han, Kim, Siskovic, and Huang (19) and by Bird (20), and the systematic treatment of Bird, Armstrong, and Hassager (18) provide considerable details.

The succinct summary included in the present work offers a brief motivation for certain of the general forms.

The oldest and the simplest viscoelastic equation, due to Maxwell (21), may be written as

$$P_{ij} + \tau \dot{P}_{ij} = G\tau \dot{\gamma}_{ij} \qquad \text{(II-13)}$$

where P_{ij} is the extra stress, associated with deformation, τ is a relaxation time, G a modulus, $\dot{\gamma}_{ij}$ is a rate of strain, and the dot denotes a time derivative. The extra stress P_{ij} and the total stress σ_{ij} are related by

$$\sigma_{ij} = - p\delta_{ij} + P_{ij} \quad . \qquad \text{(II-14)}$$

Equation (II-13) is most readily motivated by a mechanical model consisting of a spring (elastic element) and a dashpot (viscous element) in series. If τ is constant equation (II-13) may be integrated to give

$$P_{ij} = \int_{-\infty}^{t} G \exp\left(- \frac{t - t'}{\tau} \right) \dot{\gamma}_{ij}(t,t')dt' \qquad \text{(II-15)}$$

where t' denotes past time and is the variable of integration. If the previously mentioned mechanical model contains more than one Maxwell element (one Maxwell element consisting of one spring and one dashpot) then the resulting integral equation becomes

$$P_{ij} = \int_{-\infty}^{t} \sum_n G_n \exp\left(- \frac{t - t'}{\tau_n} \right) \dot{\gamma}_{ij}(t,t')dt' \qquad \text{(II-16)}$$

where the sum is over the number of Maxwell elements. The Boltzmann superposition principle (22) assumes that the stress may be obtained by adding small step strains over past time, and leads to the following constitutive equation

$$P_{ij} = \int_{-\infty}^{t} G(t - t')\dot{\gamma}_{ij}(t,t')dt' \quad . \qquad \text{(II-17)}$$

Equations (II-15) and (II-16) are special cases of (II-17), which may be considered to represent the general linear viscoelastic model. Linear viscoelasticity is restricted to describing phenomena associated with small strains and strain rates. To describe more general deformations nonlinear viscoelasticity is required.

Nonlinear viscoelastic equations may be classified as being of either the differential type or the integral type. The differential equations are of the same general form as equation (II-13). However, the dot, which denotes ordinary time differentiation for the linear models, represents one of several kinds of more complicated time derivatives in the nonlinear equations (23,24,25,26,27,28), as reviewed by Bird, Armstrong, and Hassager (18). Generally, these time derivatives may be classified as either corotational, meaning the coordinate system translates and rotates with the fluid particles, or codeformational, in which case the coordinate system

also deforms with the fluid. The analogous integral forms of these nonlinear differential models are not easily obtained; however, Bird, Armstrong, and Hassager (18) have presented several of the corresponding pairs.

A very general method of obtaining integral forms of viscoelastic equations has as its basis the theory of functionals. The fundamental assumption on which the rheological formulation rests is that the stress may be expressed as a functional over the strain history. An integral expansion of the functional is then carried out (29,30) with the result that the stress is given as a series of multiple integrals. While these expansions yield equations too complex to be applied directly to problems, this general technique provides a systematic, elegant method of organizing the numerous rheological models. Also, if only a few terms of the expansion are retained, it is found that many of the models are simply special cases of these general expansions, thereby providing further justification for the models. An excellent, qualitative discussion of this procedure is given by Bird, Armstrong, and Hassager (18).

Another method of generating viscoelastic equations involves generalizing the equations of nonlinear elasticity such that time effects are introduced. This method, due to Bernstein, Kearsley, and Zapas (31,32) results in equations equivalent to the following modified form of equation (II-3)

$$\sigma_{ij} = -p\delta_{ij} + 2\int_{-\infty}^{t} [\frac{\partial U}{\partial I} c_{ij}^{-1} - \frac{\partial U}{\partial II} c_{ij}]dt' \qquad \text{(II-18)}$$

where U denotes a time dependent strain energy function. Much of the current integral, viscoelastic theory may be summarized by the following modification of equation (II-18) (19,33,34,35)

$$\sigma_{ij} = -p\,\delta_{ij} + \int_{-\infty}^{t} [m_1 c_{ij}^{-1}(t,t') - m_2 c_{ij}(t,t')]dt' \qquad \text{(II-19)}$$

where m_1 and m_2 are memory functions and $c_{ij}^{-1}(t,t')$ and $c_{ij}(t,t')$ are relative Finger and Cauchy strain tensors. Several forms have been suggested for the memory functions (19,31,36,37,38); generally these functions depend on the past time t', the present time t, and various invariants of the strain and deformation rate tensors. For many problems, m_2 may be taken equal to zero. A simple form for m_1, in terms of either discrete or continuous relaxation spectra is

$$m_1(t - t') = \sum_n \frac{G_n}{\tau_n} \exp(-\frac{t - t'}{\tau_n}) \qquad \text{(II-20)}$$

or

$$m_1(t - t') = \int_{-\infty}^{\infty} \frac{H(\tau)}{\tau} \exp(-\frac{t - t'}{\tau}) d\ln\tau \qquad \text{(II-21)}$$

where $H(\tau)$ is the continuous relaxation spectra.

The viscoelastic theory presented thus far is isothermal, inasmuch as it is restricted to experiments conducted at constant temperature. Experimental data from different temperatures may be correlated

through the use of shift factors which express the temperature dependence of the relaxation time by shifting a reference relaxation time with the equation

$$\tau = \tau_r a_T(T) \tag{II-22}$$

where τ_r is the relaxation time at a reference temperature, T_r, and $a_T(T)$ is a shift factor. The explicit forms of the shift factors will be discussed later in this chapter. For the present it is noted that if the temperature is changing with time, then τ also changes with time through equation (II-22); in this case modifications of the previous equations are necessary. The nonisothermal treatment was first considered by Morland and Lee (39), who generalized the linear Maxwell model to include nonisothermal effects. A nonlinear, nonisothermal differential model was devised by Marrucci (40) and applied to the melt spinning process by Fischer and Denn (41). A nonlinear, nonisothermal integral model has been formulated by Matsui and Bogue (42,43,44) and applied to several nonisothermal rheological studies (43,44,45,46,47). This latter model may be expressed as

$$\sigma_{ij} = -p\,\delta_{ij} + \int_{-\infty}^{t} \sum_n \frac{G_n}{\tau_n(t')} \exp\left[-\int_{t'}^{t} \frac{dt''}{\tau_n(t'')} \right] c_{ij}^{-1}(t,t')dt' \tag{II-23}$$

where $\tau_n(X)$ is shorthand for $\tau_n(T(X))$; that is the τ_n depend on the

temperature which depends on the time. In addition to being temperature dependent, the τ_n were taken to be a function of the deformation rate through its second invariant. Further details and additional models may be found in the review articles of Pearson and McIntire (48) and White (49). More recently, Gupta and Metzner (50) have generalized a molecular model of dilute solution rheology to include nonisothermal effects, and then applied this model to the nonisothermal uniaxial extension of polymer melts.

Finally, it is noted that all of the viscoelastic theory presented so far is restricted to incompressible materials. As mentioned earlier, this restriction becomes increasingly important as the temperature approaches T_g.

B. THE GLASS TRANSITION TEMPERATURE

One of the striking characteristics of polymer behavior is the glass transition temperature, T_g. As a polymer is cooled through its glass transition, rather abrupt changes occur in several properties including the thermal coefficient of expansion, the heat capacity, the compressibility, and the mechanical properties, notably the modulus (51,52,53,54). This summary only briefly considers some of the highlights of the nature of the glass transition and the glassy state; further details are available in the book edited by Haward (55) and the reviews of Grest and Cohen (56) and Tant and Wilkes (57).

The usual operational definition of T_g is the temperature (or narrow temperature range) at which the thermal coefficient of expansion undergoes a sharp change (58); this, of course, corresponds to a change in the slope on a specific volume versus temperature plot. Above T_g the polymer molecules are able to quickly respond, through rearrangements, to temperature and pressure changes. At temperatures less than T_g the configurational rearrangements of the polymer chain backbones are extremely slow; for most practical purposes the polymer appears to be a solid. Much of this behavior may be qualitatively explained through the idea of free volume, which will be discussed in detail in the following section. For now it is noted that many properties of liquids are consistent with the presence of free volume, which appears as "holes" at the molecular scale and through which molecular rearrangements may readily occur (59).

A major difficulty encountered in dealing with the glass transition is that the value of T_g is dependent on the cooling rate, higher cooling rates leading to increased values for T_g. Several investigators (47,53,54,60,61) have reported a shift in T_g with cooling rate. Specifically, Fox and Flory (60) found that T_g increased from 5 to 10°C when the experimental cooling period was decreased from 24 hours to 5 minutes. Also, Rusch (54) indicated that T_g decreased by 3°C when the cooling rate was decreased by a factor of ten. Furthermore, Carey, Wust, and Bogue (47) have

reported that T_g increased by as much as 16°C when the cooling rate was increased from 0.003 to 4.5°C/sec.

These experimental data clearly imply that the observed glass transition temperature is a kinetic phenomenon. The prior definition of T_g as the temperature at which the thermal coefficient of expansion suddenly changes implies that it is a second-order transition. The controversy over whether T_g is a kinetic phenomenon as opposed to a true thermodynamic transition has not been resolved (62). However, it is noted that the definition and the experimental data may be reconciled by postulating that the second order transition is a limiting value of T_g, obtainable only at infinitely slow cooling rates. On the other hand, the experimentally observed glass transition temperatures are the temperatures at which the time scales of the molecular rearrangement processes become comparable to the time scales of the measurements.

C. AGING PHENOMENA

As discussed previously, the relaxation of frozen-in nonequilibrium properties, produced by cooling the polymer through its glass transition, results in the aging of the sample. It is important to distinguish between frozen-in nonequilibrium properties, such as free volume and molecular orientation, and residual stresses. The former are present in small, homogeneous samples through which there is no significant temperature gradient. In contrast, residual

stresses result directly from temperature gradients present in large samples (63,64). Residual stresses are not considered in the present work.

Free Volume and Volume Aging

The concept of free volume is very useful in describing the properties of liquids (59). The thermal coefficient of expansion of liquids, polymeric or otherwise, primarily represents the creation of additional free volume with increasing temperature. The substantially smaller values, characteristic of crystalline solids and amorphous glasses, arise from interatomic or intermolecular interactions. The difference between the total specific volume, v, and the occupied volume, v_g, may be defined as the free volume, v_f (54,60,62,65,66,67)

$$v_f = v - v_g \quad . \tag{II-24}$$

The occupied volume (denoted above as v_g to imply the glassy volume) may be thought of as that portion of the total volume actually taken up by the molecules. The free volume is comprised of an equilibrium portion, v_{fe}, and a nonequilibrium portion, v_{fn} (54)

$$v_f = v_{fe} + v_{fn} \quad . \tag{II-25}$$

Some of the relationships between these various volumes and the glass transition temperature are illustrated in Figure 1. The temperature

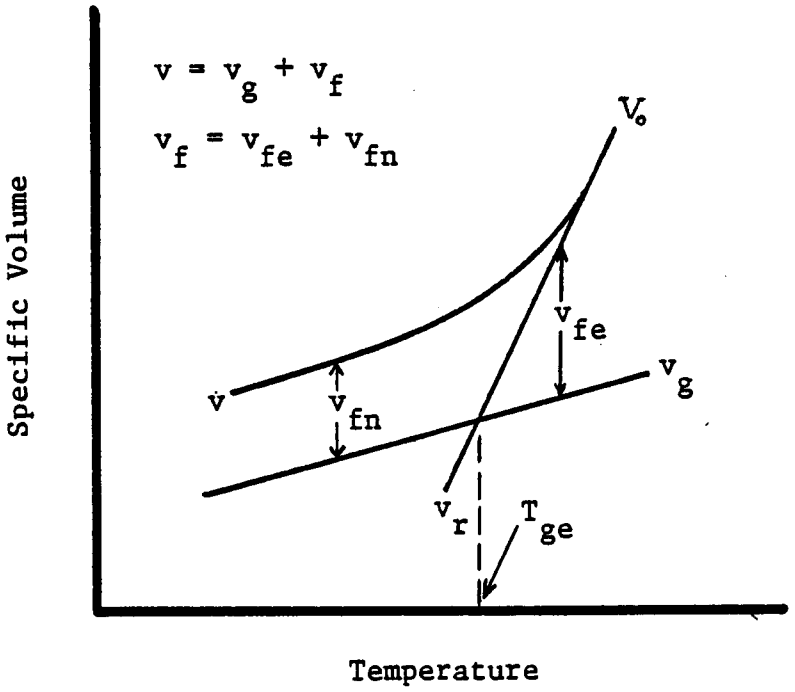


Figure 1. Schematic representation of the free volume concept.

denoted by T_{ge} in Figure 1 represents the equilibrium T_g; this is the glass transition temperature that would be observed at an infinitely slow cooling rate. It is noted that at temperatures less than T_{ge} there is no equilibrium free volume, while at temperatures greater than T_{ge} the equilibrium free volume is the difference between the rubbery or liquid volume, v_r, and the glassy or occupied volume, v_g.

To define the equilibrium volumes v_r and v_g mathematically, it is necessary to define an equilibrium reference volume v_o. For convenience, v_o is chosen at a reference temperature T_o, well above the glass transition. The equations for the v_r and v_g lines, and for the equilibrium free volume are

$$v_r = v_o - \alpha_r(T_o - T)v_o \tag{II-26}$$

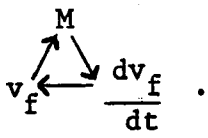
$$v_g = v_o - \alpha_r(T_o - T_{ge})v_o - \alpha_g(T_{ge} - T)v_o \tag{II-27}$$

$$v_{fe} = v_r - v_g = v_o(\alpha_r - \alpha_g)(T - T_{ge}) \tag{II-28}$$

where α_r and α_g are the coefficients of expansion of the rubber and the glass, respectively. The effective coefficient of expansion of the holes, or the free volume, is $\Delta\alpha = \alpha_r - \alpha_g$.

If a polymer is cooled through its glass transition at a finite cooling rate, it will contain frozen-in, nonequilibrium volume. The subsequent approach to equilibrium, referred to as physical aging,

occurs through molecular redistribution. Struik (67,68) has postulated a cyclic process interelating the free volume, v_f, the molecular mobility, M, and the aging, (the change of free volume with time) $\frac{dv_f}{dt}$. The free volume determines the mobility, while the mobility governs the rate at which the free volume changes; schematically,



As the temperature is lowered, the mobility decreases and below a certain temperature M becomes sufficiently small so that v_f almost stops decreasing with temperature. This is the glass transition temperature.

Volume aging has been extensively studied both from an experimental and theoretical viewpoint. The recent review of Tant and Wilkes (57) provides considerable detail. Alfrey, Goldfinger, and Mark (69) report that the glass transition temperature of polystyrene varied with the cooling rate, and that the volume decreased with time after the quench. They explain their results qualitatively utilizing free volume concepts. Goldbach and Rehage (70,71) have performed volume aging experiments on polystyrene under isothermal-isobaric conditions after the application of temperature and pressure jumps. The observed behavior could not be explained using a single retardation time, but instead it was necessary to assume a retardation time distribution. Struik (67,68) has studied the

effect of free volume and volume aging on the mechanical properties of polymers. He has shown that in many cases the volume aging effects on the mechanical properties is dominant over temperature effects, even if significant temperature changes are involved. Rusch (54) has measured the volume contraction of polystyrene and polymethylmethacrylate between -20°C and +95°C over a time span of about three hours. He used the data to estimate the amount of frozen free volume present in the glass and to determine the temperature dependence of the shift factor (see equation (II-22)). He also introduced an equivalent temperature, which is a free volume modified temperature, and used this concept to explain much of the data. Rusch and Beck (61) also have used an equivalent temperature to interpret the yielding behavior of polymethylmethacrylate. Kovacs, et al. (53,66,72,73,74,75,76,77) have extensively studied free volume and volume aging and their effect on mechanical properties. Much of Kovacs' effort has involved the development of rate equations to describe the relaxation of free volume. If the restriction of constant pressure is imposed, the rate equation may be written (73,75)

$$\frac{dv}{dt} = - \frac{(v - v_\infty)}{\tau} - \alpha_g R v_\infty \qquad \text{(II-29)}$$

where v_∞ denotes the equilibrium volume and R is the cooling rate, $R = - \frac{dT}{dt}$. A number of other researchers (52,54,70,71,78,79,80) have used equations similar to (II-29). Equations in the form of (II-29) are referred to by Kovacs (77) as one parameter models,

inasmuch as the recovery is accounted for by a single relaxation mechanism involving one relaxation time. More recently, multiple parameter models have evolved (77). These consist of a set of differential equations, each of the form of equation (II-29), which must be solved simultaneously.

The use of any of these rate equations, as well as the application of the viscoelastic constitutive equations of the prior section, requires knowledge of the relaxation time τ. In the simplest case, τ is taken to be a function of temperature only; the functional dependence is stated by equation (II-22) where $a_T(T)$ is a temperature dependent shift factor. At temperatures above T_g the shift factor was empirically found to be given by the so-called Williams, Landel, and Ferry equation (81) (the WLF equation)

$$\log a_T(T) = \frac{- C_1(T - T_r)}{C_2 + T - T_r} \qquad \text{(II-30)}$$

where C_1 and C_2 are constants and T_r is a reference temperature at which $\tau = \tau_r$. Equation (II-30) may be derived (62,81) from the Doolittle equation (82) which is an empirical relationship between viscosity and free volume. Rusch (54) also derived equation (II-30) from arguments based on the probability of molecular rearrangement occurring. Equations (II-22) and (II-30) may be used to correlate data obtained from isothermal experiments at different temperatures. These equations may also be employed for nonisothermal calculations where the temperature depends on time.

Normally, the relaxation time appearing in the rate equations is taken to be a function of free volume as well as temperature. In this case, equation (II-22) is replaced by

$$\tau = \tau_r a_{TV} \tag{II-31}$$

where a_{TV} is a shift factor which depends on both free volume and temperature. Rusch (54), again based on probability arguments, derived the following equation for a_{TV}

$$\log a_{TV} = \frac{- C_1(T_e - T_r)}{C_2 + T_e - T_r} \tag{II-32}$$

where T_e is an "equivalent temperature" depending on both the temperature and free volume. Equation (II-32) is appealing in that it is the same form as the WLF equation and thus represents an extension of the WLF equation to lower temperatures. Kovacs (77) writes the shift factor as a product of a temperature dependent factor and a free volume dependent factor

$$a_{TV} = a_T a_V \tag{II-33}$$

where a_T and a_V are given by

$$a_T = \exp[- \theta(T - T_r)] \tag{II-34}$$

$$a_V = \exp\left[- (1 - x)\theta \frac{v - v_\infty}{v_\infty \Delta\alpha} \right] \qquad \text{(II-35)}$$

where θ, x, and $\Delta\alpha$ are material parameters which all may depend on temperature. The notation a_V is somewhat deceiving in that a_V is a function of both temperature and free volume, and thus it represents the structure dependence of τ only at constant temperature.

Orientation and Orientation Aging

If a polymer is being deformed as it is cooled through its glass transition molecular orientation will be frozen into the sample. The considerable attention afforded to the study of orientation in polymers stems from its significant effect on mechanical properties. The properties of oriented polymers have been reviewed in detail in a book edited by Ward (83). Much of the research effort has focused on crystalline polymers; however, only amorphous polymers will be considered in this discussion.

Generally it is found that high degrees of orientation may be frozen into the glassy product by rapidly deforming the melt at temperatures slightly above T_g and then quickly cooling through the glass transition. Oda, White, and Clark (84) and Carey, Wust, and Bogue (47) have demonstrated that the orientation (stress) induced in the melt may be used as the characterizing variable for the subsequent glassy sample. A number of investigators have reported enhanced mechanical properties due to the frozen-in orientation. Nielsen and Buchdahl (85), Matsumoto and Bogue (86), and Carey,

Wust, and Bogue (47) have reported increases in the modulus and tensile strength of polystyrene with increasing orientation. Also, Thomas and Cleereman (87) and Matsumoto, Fellers, and White (88) have investigated the enhancement of the mechanical properties of biaxially stretched polystyrene. Further details may be found in the book edited by Ward (83).

Orientation aging refers to the decay of molecular orientation with time; while this process is very slow at room temperature, it may become quite rapid if the temperature is brought near T_g. Rudd and Gurnee (89) have studied the shrinkage of oriented polystyrene and have introduced the idea that the relaxation process involves relaxation of both orientation (rubbery) and Hookean (glassy) components. However, at temperatures near T_g the latter relaxes very quickly and thus long term relaxation is attributed to orientation. Andrews (90) monitored both the birefringence and shrinkage of oriented polystyrene fibers and has shown that at temperatures near T_g the fibers will relax to an unoriented state. His studies also indicated that at temperatures much less than 10°C under T_g the relaxation was very slow, while if the temperature surpassed T_g by more than 10°C the decay was very rapid. Jones (91) has investigated the relationship between orientation and birefringence; he concluded that, especially at temperatures above T_g, the orientation relaxation leads to shrinkage which is proportional to the birefringence exhibited by the material. Tanabe and Kanetsuna (92) also studied the relationship between birefringence and shrinkage of

oriented polystyrene fibers under external loads. Furthermore, Ito, Horie, and Kobayashi (93) have measured the shrinkage of oriented polystyrene at a variety of temperatures. They observed that at temperatures above 80°C a decrease in birefringence was accompanied by shrinkage, although the former preceeded the latter; however, at temperatures less than 80°C the birefringence decayed but the samples did not shrink.

In related studies at The University of Tennessee, Boateng (94) has investigated the effects of temperatures below T_g on the birefringence. Polystyrene was found to exhibit constant birefringence if it were constrained at constant length; for unconstrained samples the birefringence varied. Polymethylmethacrylate showed a varying birefringence regardless of whether or not it was constrained. Potnis (95) has measured the shrinkage and the birefringence of highly oriented polystyrene fibers under varying external loads at three temperatures somewhat less than T_g. He concluded that the birefringence decay and shrinkage both proceed at similar rates, although the latter consistently lags behind the former by a small amount. His experimental technique and his results will be considered in more detail later in this thesis.

CHAPTER III

EXPERIMENTAL

The free volume aging of polystyrene was investigated at 90°C, 70°C, and 25°C following a rapid quench from about 120°C. A method was developed to correct for aging during the time the samples were settling in the density gradient column. Details of the experimental procedure will now be presented.

A. MATERIAL AND SAMPLE PREPARATION

The material investigated was a typical commercial polystyrene (Shell TC3-30) furnished by the Shell Chemical Company. It has a broad molecular weight distribution with a number average molecular weight, M_n, of 6.1×10^4 and a weight average molecular weight, M_w, of 2.8×10^5 giving $\frac{M_w}{M_n} = 4.6$. This particular polymer has been extensively investigated in prior work (47). The samples were made by extruding the polystyrene from an Instrom capillary rheometer at a low crosshead speed (0.002 in./min.) through a 0.03 in. die. The cylindrical samples thus formed had diameters of approximately 0.5 mm. They were annealed several hours at 130°C prior to use.

B. EQUIPMENT AND PROCEDURE

Equipment and Quenching Procedure

The oven used for heating the samples prior to quenching has been described in detail elsewhere (43,95,96). Basically, it is a

"clam shell" device designed for use in conjunction with an Instron tensile tester. The maximum temperature variation between the top and bottom of the oven (about 20 in.) is about 1°C. The aging chamber employed for the high temperature aging was a standard Fisher Isotemp lab oven. The maximum temperature variation between the top and bottom of this oven is about 4°C; however, during aging the samples were placed in a horizontal position to improve the temperature uniformity. The control sensitivity of the lab oven is about 1-2°C. The free volume aging was determined by monitoring the density over time in a density gradient column made from ethylene glycol-water solutions.

The most logical way to perform an aging experiment at high temperature would be in a density gradient column operating at the temperature of interest. Therefore, considerable effort was devoted to the construction of such a column; however, the density gradient at these high temperatures invariably decayed within a few hours. Nevertheless, for future reference, the procedure employed for filling the high temperature density gradient columns, as well as some of the difficulties encountered, will be discussed.

It is obvious that the column must be operated under isothermal conditions. The normal procedure employed at room temperature is to pump water through the density gradient column jacket and to regulate the temperature of the water to the desired precision. As the temperature is increased this process clearly becomes more difficult; it would probably be necessary to insulate the column and

increase the flow rate of the circulating water to minimize heat losses. As an attempt to overcome these difficulties a smaller column was constructed. The advantage of the smaller column is that it could readily be immersed in a constant temperature bath, thus eliminating the need for insulation and a circulating fluid. The small column had a length of about 40 cm and a diameter of about 6.0 cm. The bath, operating at 80°C, was isothermal to within 0.1°C between the bottom and top of the column. This temperature difference was believed to be sufficiently small so as not to induce a density gradient.

However, the temperature control proved to be only one of the problems encountered. Another difficulty was that the coefficients of expansion of the two fluids used to construct the column were different; this fact alone led to mixing as the temperature of the column was increased. A judicious choice of fluids such that the coefficients of expansion are nearly the same helps eliminate this problem. In the present work water-sodium bromide solutions were used. Prior to filling the column it was necessary to boil the solutions in order to expel dissolved air; this was found to be very important because of the high temperatures involved.

Several questions arise concerning the actual procedure used to fill the column. Better results were usually obtained if the column were heated and then filled as opposed to making the column prior to heating it. Also, it was found that less mixing occurred during the filling procedure if the column were filled from the

bottom by introducing the less dense solution first; this is opposite from the method normally employed.

Finally, however, the most serious problem that could not be resolved was the rapid disappearance (24 hours maximum) of the density gradient at temperatures above about 60°C. In retrospect, perhaps part of the problem was the small column or, at least the small length to diameter ratio of the column; if one desires to build a short column then its diameter should also be reduced.

Lacking a density gradient column operable at elevated temperatures the high temperature aging was carried out in the standard lab oven mentioned earlier. The experimental procedure employed is outlined below. Polystyrene samples, about six inches long, were suspended from one end in the Instron oven for one hour at 118°C. Thermocouples were placed in the oven at each end of the sample and the temperature recorded; the temperature was isothermal to within 1°C over the six inch sample length. The sample was presumed to be in equilibrium after one hour at 118°C. At the end of the heating period the sample was quickly removed from the oven and placed in ice water; a quantitative estimate of the cooling rate during the ice water quench was made and will be discussed later. After removing the sample from the ice water a piece about 0.5 cm long was placed in the density gradient column; the rest of the sample was placed in the lab oven at the aging temperature. Approximately once per day (more often initially) a 0.5 cm piece was cut and placed in the density gradient column. The room temperature

aging was conducted outside of the density gradient column in order to be as similar as possible to the higher temperature aging. With the exception of the initial density, all density readings were taken after the samples had been in the column for three hours. The method used to obtain the initial density will be discussed later.

Obviously, the most practical way to carry out a room temperature aging experiment is to monitor the density as a function of time for a single sample which is left in place in a density gradient column. However, as mentioned above, in order to be consistent with the higher temperature aging, the room temperature aging was performed outside of the density gradient column. This procedure presents two problems. First, each density data point is obtained from a different sample; in order to obtain reasonably consistent results it was necessary to use samples of uniform length (0.5 cm was chosen as a convenient length) and to take all density readings after a constant time in the column. Secondly, some assumption must be made regarding the relationship between the measured density and the density at the aging temperature. It has been assumed in treating the data that the measured density is related to the density at the aging temperature through a glassy coefficient of expansion; specifically

$$\rho_{meas} = \left[\frac{1}{\rho_{age}} - \alpha_g (T_{age} - T_{meas}) v_o \right]^{-1} \qquad \text{(III-1)}$$

where ρ_{meas} and ρ_{age} are the measured and aging densities respectively at the measuring and aging temperatures T_{meas} and T_{age}. Clearly, this supposition is invalid if significant aging occurs while the polymer is cooled from the aging to the measuring temperature. Therefore, the basis for the assumption is that the time of cooling is small (or, equivalently, the cooling rate is high) compared to the relaxation time. Consequently, the reliability of equation (III-1) diminishes as the temperature approaches T_g. Experimentally it was found that the measured densities of samples aged at 70°C were independent of whether the samples were cooled through an air quench as opposed to an ice water quench. However, if the samples were aged at 90°C, the measured densities were dependent on the cooling rate; those which were ice water quenched had somewhat lower densities. These data suggest that equation (III-1) is valid at 70°C but begins to lose validity at temperatures near 90°C.

A quantitative estimate of the cooling rate during the ice water quench was made with small thermocouples coated with polystyrene. The thickness of the polystyrene coat was approximately equal to the diameter of the samples (0.5 mm). The polystyrene coated thermocouples were heated in the Instron oven prior to being quenched in ice water. A temperature-time plot was recorded. The cooling rate was estimated from the initial slope of the

temperature-time plot

$$R \cong -\frac{\Delta T}{\Delta t} = 160°C/sec. \qquad \text{(III-2)}$$

Aging and Settling in the Density Gradient Column

It is to be expected that quenching samples at a high cooling rate will lead to a considerable amount of free volume being frozen into the glassy polymer. This large amount of free volume results in small relaxation times and thus rapid aging, particularly immediately after the quench. When a small sample is placed in the density gradient column it takes several hours for it to settle to a point where the density may be read; during this time the sample is obviously aging. Figure 2 shows a plot of the apparent density versus time for two samples. The apparent density is the density read directly from the density gradient column. The "well aged sample" had aged for about ten days following an ice water quench, while the "recently quenched sample" had been placed in the column immediately following the quench. After about one hour the first sample had reached a reasonably constant equilibrium position; however, the apparent density of the second sample continued to increase indicating that it was aging at a significant rate in addition to settling in the column. If the density at the end of the quench (the initial density) is simply taken to be the apparent density after several hours in the column, a notable amount of the free volume aging is being neglected. Because of this concern and

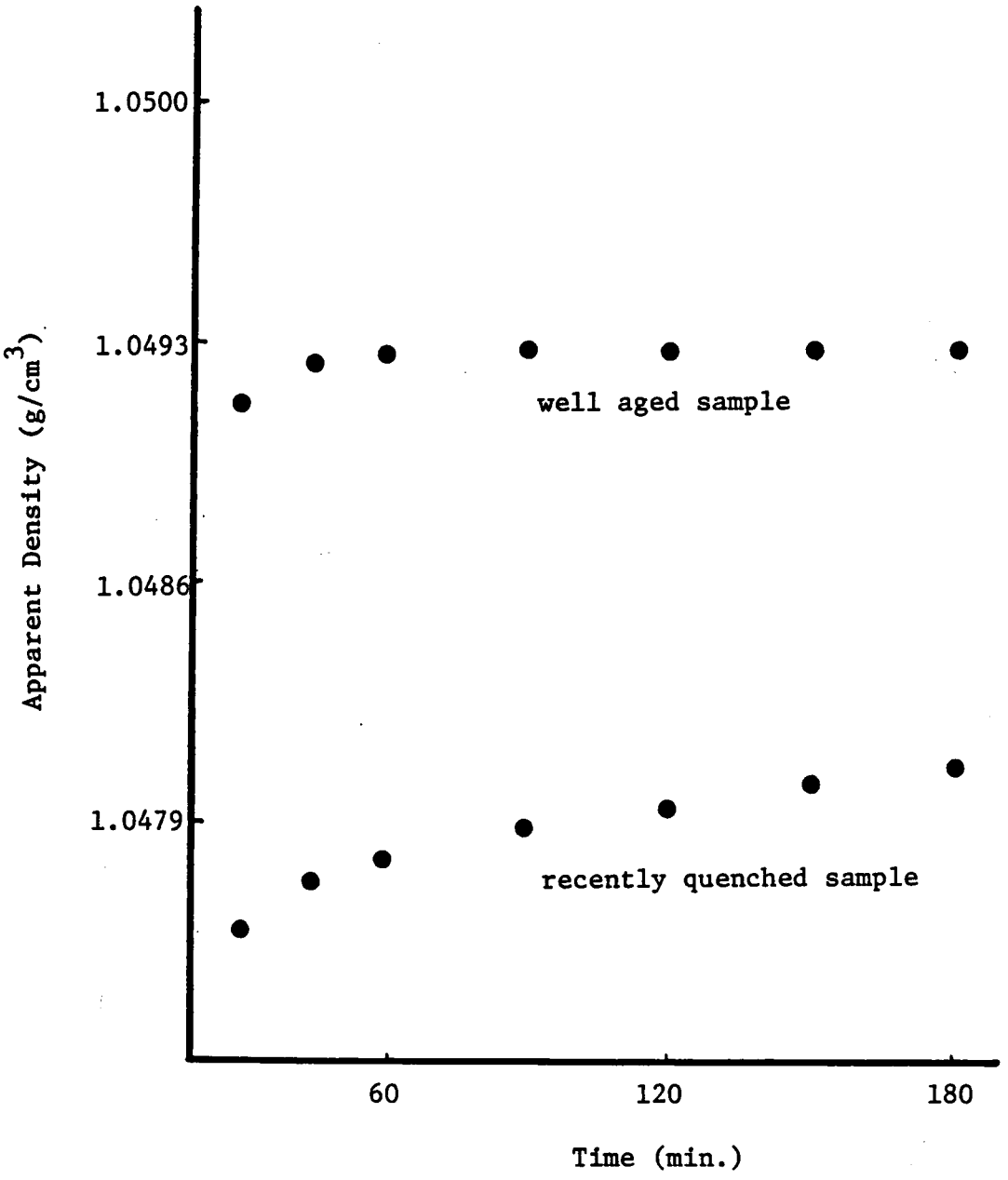


Figure 2. Apparent density as a function of time in the density gradient column for a recently quenched sample and a well aged sample.

a desire to obtain the initial density as accurately as possible an analysis of settling and initial aging was undertaken.

The basis for the analysis is Stokes' settling law which may be written (97)

$$U = \frac{2gR_p^2}{9\mu} (\rho - \rho_f) \qquad \text{(III-3)}$$

where U is the settling velocity, g is the acceleration due to gravity, R_p is the radius of the spherical particle, μ is the viscosity of the fluid in which the particle is settling, and ρ and ρ_f are the densities of the particle and fluid respectively. If the settling particle is cylindrically shaped and is aging, and if the fluid density varies with height in the density gradient column, a reasonable modification of equation (III-3) is

$$U = \frac{dZ}{dt} = \beta(\rho(t) - \rho_f(Z)) \qquad \text{(III-4)}$$

where Z is the column reading and β is a constant which will be determined from experimental settling data. Comparison of equations (III-3) and (III-4) shows that β is related to the "effective radius" of the settling particle and that β should increase with decreasing fluid viscosity. Stokes' settling law was derived for spherical particles; to demonstrate that it is feasible to use equation (III-4) for cylindrical particles it has been applied to some settling data obtained for well aged samples. In this case

$\rho(t)$ is essentially constant and

$$\rho_f(Z) = aZ + b \qquad \text{(III-5)}$$

where a and b are the density gradient column constants. Substituting equation (III-5) into (III-4), taking $\rho(t)$ to be constant, and solving the resulting equation with the condition $Z(0) = 0$ gives

$$Z = \frac{\rho - b}{a} [1 - \exp(- a\beta t)] \quad . \qquad \text{(III-6)}$$

Figure 3 shows a fit of settling data obtained using equation (III-6) with the following numerical values: $\rho = 1.0488$ g/cm^3, $b = 1.0328$ g/cm^3, $a = 0.0003771$ g/cm^4, and $\beta = 580$ cm^4/g min.

Consideration is now given to the problem of simultaneous settling and aging; this requires a function for $\rho(t)$ to use in equation (III-4). Ideally, one would solve a rate equation, such as equation (II-29), taking τ to be constant, to obtain the $\rho(t)$ function. However, substituting the functional form for $\rho(t)$ so obtained into equation (III-4) leads to an equation which requires numerical integration. To avoid the complication of numerical integration the function $\rho(t)$ is obtained as the solution of

$$\frac{d\rho}{dt} = \frac{\rho_\infty - \rho}{\tau} \; ; \; \rho(0) = \rho_o \qquad \text{(III-7)}$$

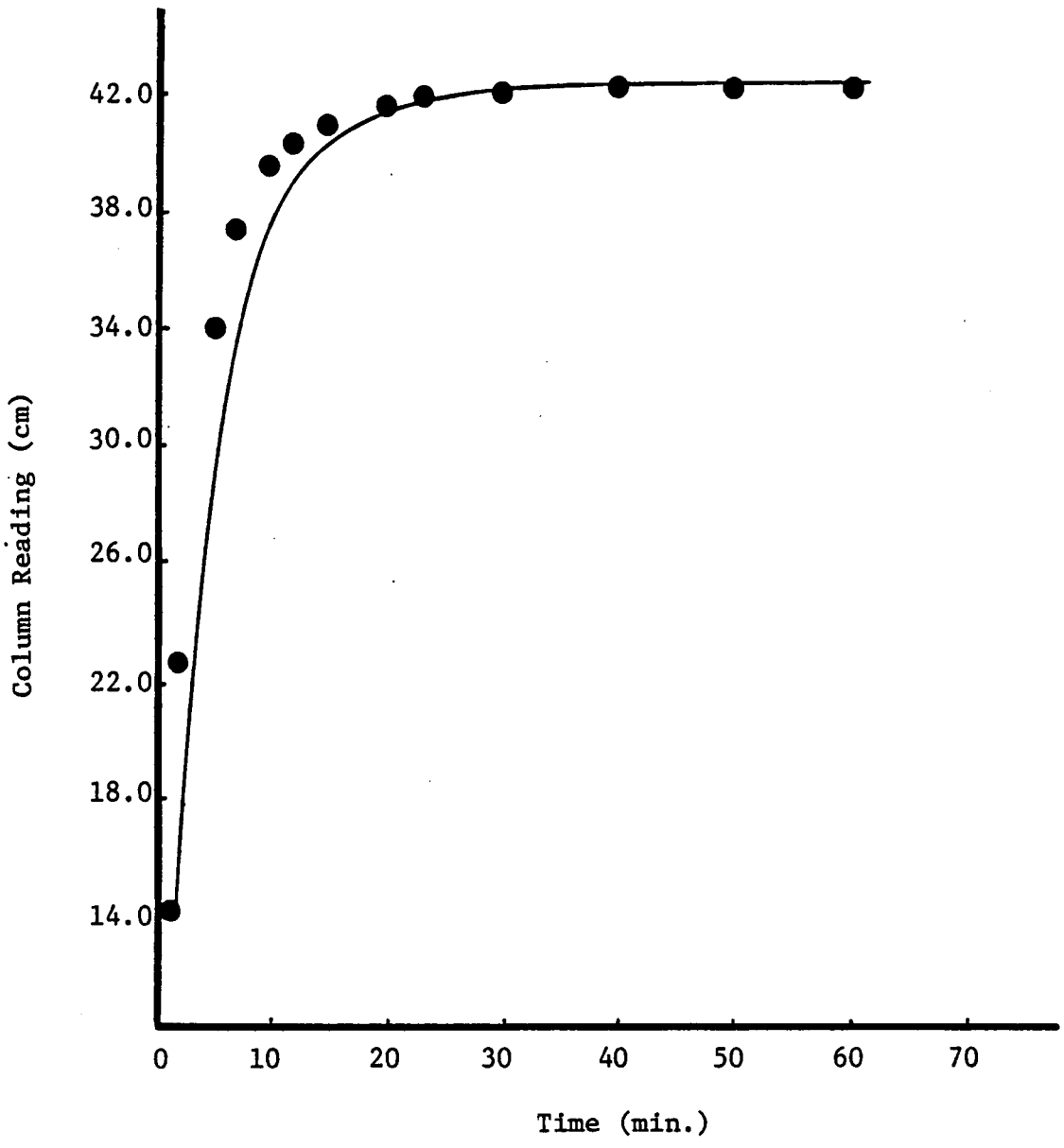


Figure 3. Theoretical fit of setting data for a well aged sample.

where ρ_o is the initial density of the particle and ρ_∞ is the equilibrium density. The solution to equation (III-7) is

$$\rho(t) = \rho_\infty + (\rho_o - \rho_\infty)\exp(-\frac{t}{\tau}) \quad . \tag{III-8}$$

Substituting equations (III-8) and (III-5) into (III-4) and solving with the condition $Z(0) = 0$ gives

$$Z = \frac{\rho_\infty - b}{a}[1 - \exp(-a\beta t)]$$

$$+ \tau \frac{\rho_o - \rho_\infty}{a\tau - 1/\beta}[\exp(-\frac{t}{t}) - \exp(-a\beta t)] \quad . \tag{III-9}$$

Ideally one would use equation (III-9) in conjunction with settling data to obtain the initial density; however, the equation, as written, is too complex to be of practical use. Some simplification of equation (III-9) is possible considering the numerical values of a and β. Using the previously determined values of a and β shows that, for settling times greater than one hour,

$$\exp(-a\beta t) < 2 \times 10^{-6} \tag{III-10}$$

and

$$1/\beta = 0.0017 \quad . \tag{III-11}$$

Using these numerical values, and assuming a relaxation time of about one hour, equation (III-9) may reasonably be reduced to

$$Z = \frac{\rho_\infty - b}{a} + \frac{\rho_o - \rho_\infty}{a} \exp\left(-\frac{t}{\tau}\right) \quad . \qquad \text{(III-12)}$$

Equation (III-12) is equivalent to equation (III-8); the settling data indicate that these equations are applicable only for settling times greater than about one hour. Equation (III-12) may be written

$$\ln(\rho_\infty - aZ - b) = \ln(\rho_\infty - \rho_o) - \frac{1}{\tau} t \qquad \text{(III-13)}$$

which suggests that a plot of $\ln(\rho_\infty - aZ - b)$ versus t should be linear, and that the initial density may be obtained by extrapolating to $t = 0$. The unknown equilibrium density drops out of the problem after extrapolating to $t = 0$.

C. RESULTS AND DISCUSSION

The results obtained for the initial density from the previously discussed plotting procedure and the aging data at 90°C, 70°C, and 25°C are presented in this section.

Initial Density

The initial density is obtained from a plot of $\ln(\rho_\infty - aZ - b)$ versus t. The linear portion of the plot is extrapolated to $t = 0$ from which the initial density may be obtained through equation (III-13). Figure 4 shows such a plot. The values of a and b were those listed previously and ρ_∞ was taken as 1.0505 g/cm^3. Clearly,

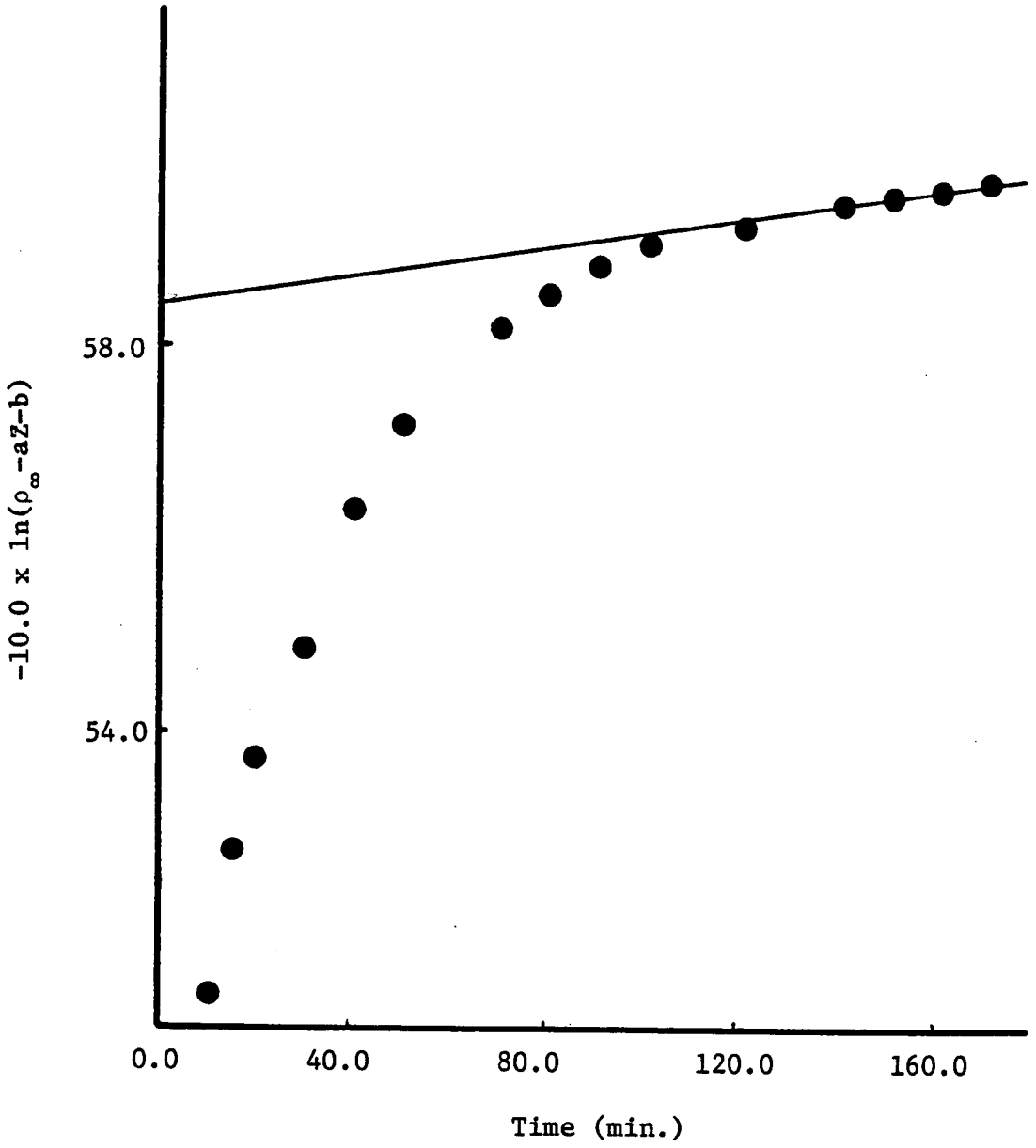


Figure 4. Extrapolation of settling data to zero time to obtain initial density.

there is some ambiguity in the extrapolation, however, even so, such a plotting technique consistently gives densities of (1.0476 ± 0.0003) g/cm^3 for samples which were quenched in ice water.

Volume Aging Data

Volume aging data have been obtained at 90°C, 70°C, and 25°C. All measurements were made at 23°C and were collected over a time span of about 500 hours. The data are presented in Figures 5, 6, and 7. The data obtained at 25°C indicates that the free volume decays rather gradually and, even after 500 hours, the aging is still continuing slowly. At 70°C, however, the free volume rapidly decays initially (the first 80 to 100 hours) and then essentially remains constant. Also, at 90°C the decay is rapid at times less than about 40 hours after which it changes very slowly. These data will be treated in Chapter V.

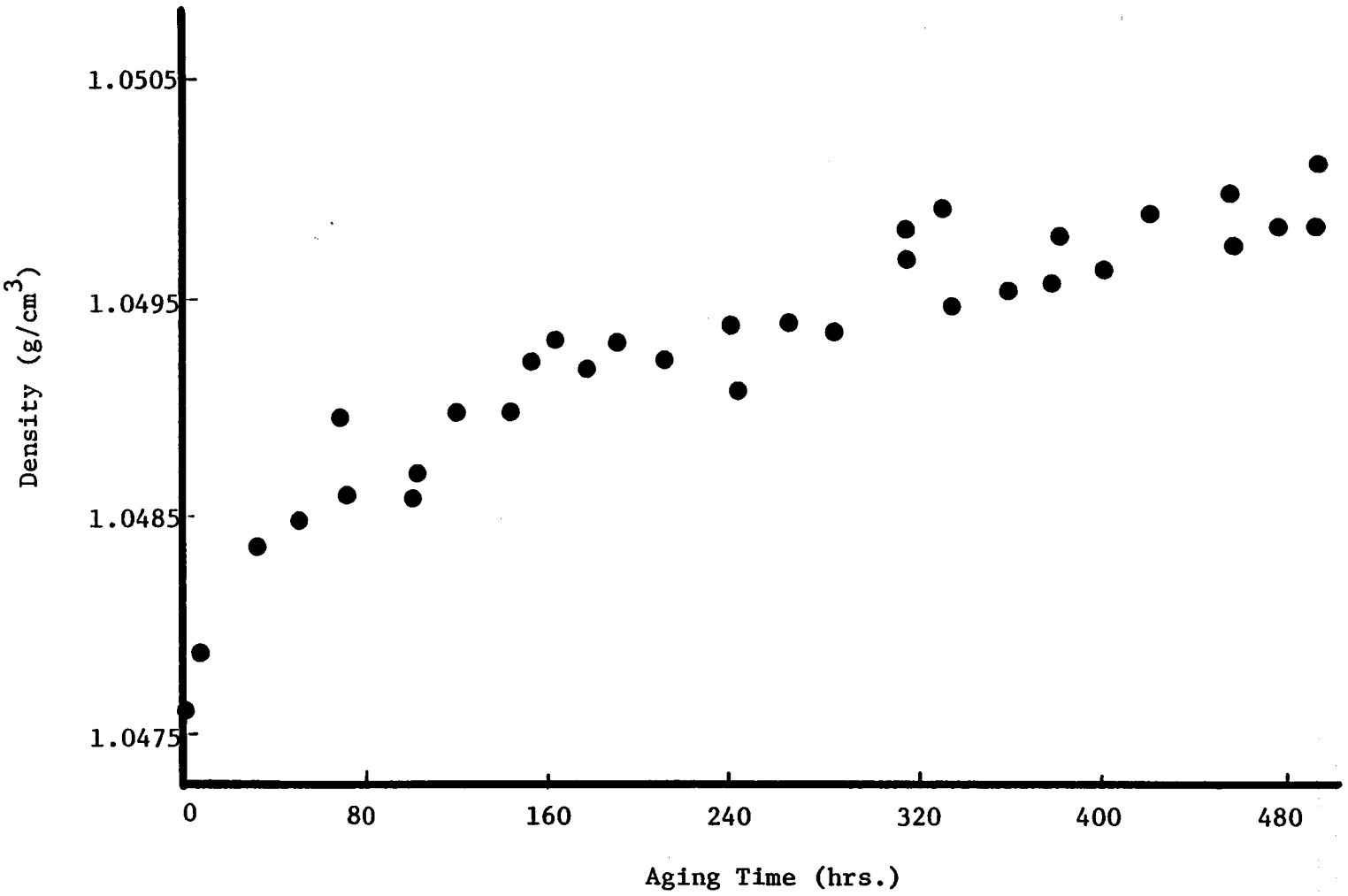


Figure 5. Volume aging data at 25°C.

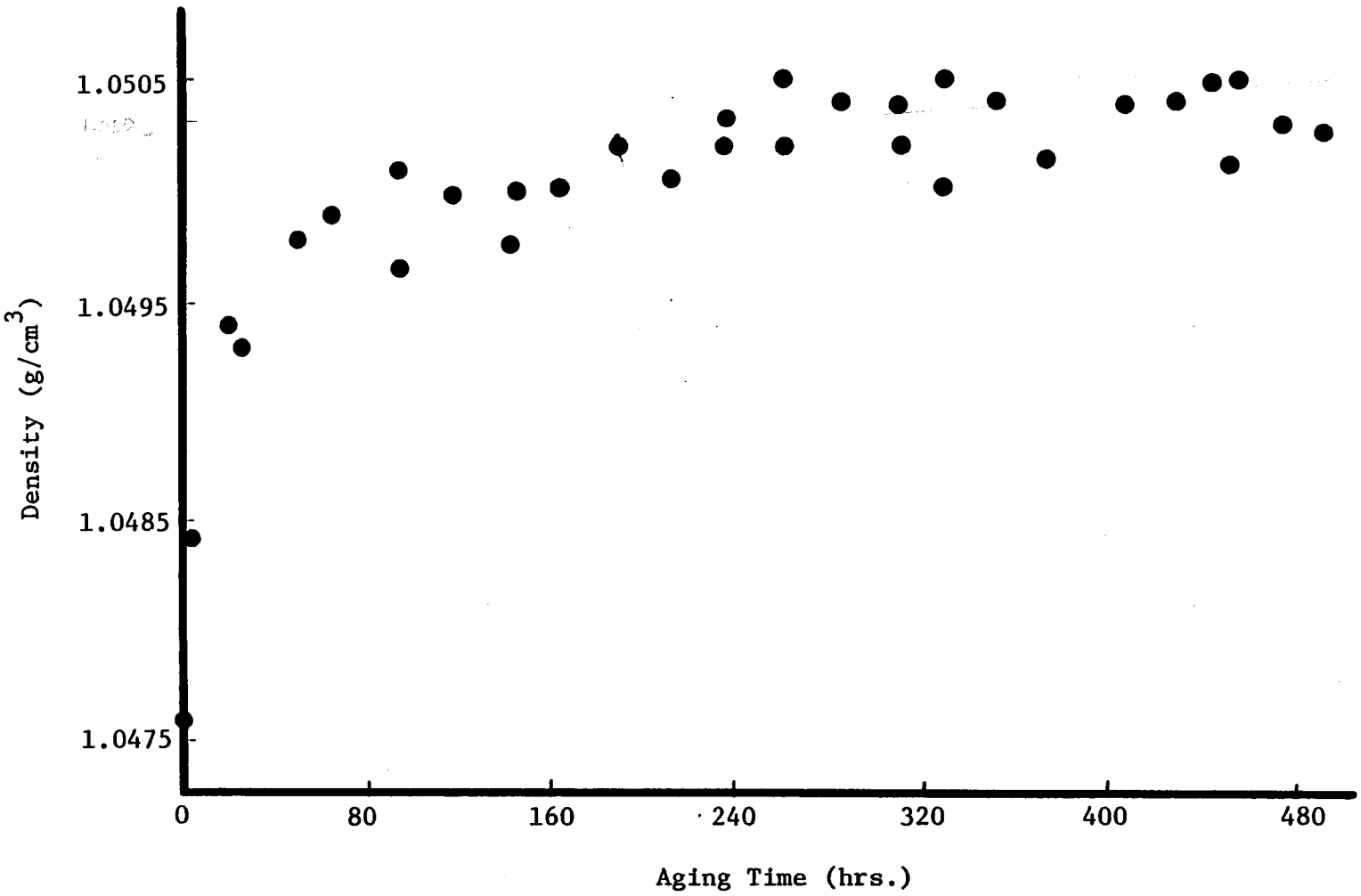


Figure 6. Volume aging data at 70°C.

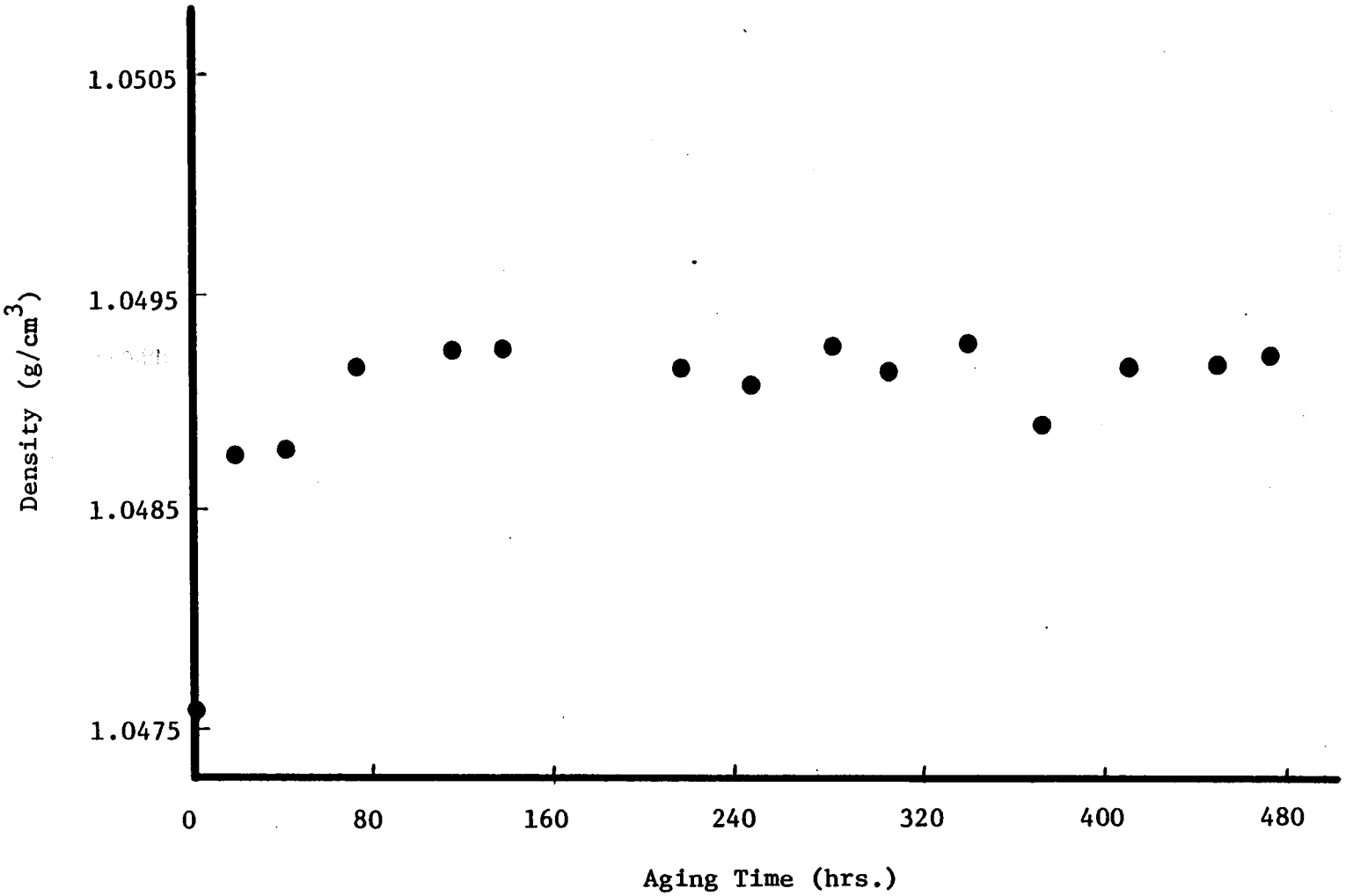


Figure 7. Volume aging data at 90°C.

CHAPTER IV

INTEGRAL STATEMENT OF THE GENERAL MODEL

In this chapter a generalized viscoelastic constitutive model, including compressible effects, is proposed. Some motivation for the equation is first considered followed by a discussion of its behavior in several special cases.

A. GENERAL INTEGRAL EQUATION

As discussed previously, viscoelastic equations, at least as they are actually applied, do not include compressible effects. Inasmuch as rubbery materials typically exhibit Poisson's ratios of about 0.5, neglecting the volume changes accompanying deformations is certainly valid at temperatures significantly above T_g. However, if the theory is to trace the polymer history from the rubbery state, through T_g, down into the glassy state, the compressible effects assume a more important role. First, glassy materials have a Poisson's ratio of about 0.3 and therefore significant volume changes are associated with deformations. Also, the phenomenon of volume aging in glasses is of considerable interest; clearly the treatment of volume aging through a constitutive model framework requires that compressible effects be included in the rheological model. Furthermore, since T_g is usually defined as the temperature at which there is a rather sudden break in the volume-temperature curve, it is obvious that compressibility should be included in describing

phenomena associated with the glass transition. Finally, since many experiments of interest involve cooling through the glass transition, it would be aesthetically pleasing to have a single constitutive model applicable both above and below T_g.

This general model should have the following characteristics. Since it is to be applicable for polymer melts it must include nonlinear strain tensors to describe large deformations. Also, since polymer melts exhibit viscoelastic behavior, time effects must be included. Finally, since it is to be employed during and below the glass transition, compressible effects are required. The equations of nonlinear elasticity, in their general form, (see equation (II-1)) satisfy the first and third of the above requirements; however, time effects are absent from these equations. Motivated by the Bernstein, Kearsley, and Zapas (31,32) (see equation (II-18)) method of introducing time effects into the equations of rubber elasticity, it would seem logical to propose a similar viscoelastic generalization of equation (II-1). The resulting viscoelastic constitutive equation would include compressible effects through the third invariant; also, a judicious choice for the strain energy function W(I,II,III) results in an equation which, when linearized, reduces to linear elasticity. However, a nonisothermal generalization introduces the difficulty that the volume base state becomes a function of temperature. If the temperature dependence of the base state is introduced in the same manner as in linear elasticity (see equation (II-10)), the resulting equations exhibit only equilibrium volume-temperature

behavior. The absence of nonequilibrium volume-temperature effects is clearly inadequate. Therefore, one is led to state a rate equation, such as equation (II-29), in integral form so that it may be incorporated into a more general viscoelastic model.

All of these considerations have led to a model which may be stated as

$$\sigma_{ij} + P\delta_{ij} + \delta_{ij}\int_{-\infty}^{t}\lambda^*(t')\frac{d}{dt'}\left[\frac{v_e(t') - v(t')}{v_o}\right]dt'$$
$$= \delta_{ij}\int_{-\infty}^{t}\lambda^*(t')\exp\left[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\right]\frac{d}{dt'}\left[\frac{v_{fe}(t')}{v_o}\right]dt'$$
$$+ \int_{-\infty}^{t}G(t')\exp\left[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\right]\frac{c_{ij}^{-1*}(t,t')}{\tau(t')}dt' \qquad \text{(IV-1)}$$

where P is the pressure, v_e is the equilibrium volume, λ^* is the bulk modulus, and c_{ij}^{-1*} is a normalized Finger strain tensor

$$\lambda^* = \lambda + \frac{2}{3}G \qquad \text{(IV-2)}$$

and

$$c_{ij}^{-1*}(t,t') = c_{ij}^{-1}(t,t') - \delta ij - \frac{2}{3}\left(\frac{v(t) - v(t')}{v(t')}\right)\delta_{ij} \quad . \qquad \text{(IV-3)}$$

The quantity c_{ij}^{-1*} has been normalized so as to be identically zero if only volume changes are occurring (throughout the treatment volume changes are linearized) and to be nonzero if some noniso-tropic change is also occurring. The other variables in equation (IV-1) have been defined previously. The equilibrium volume

(v_r or v_g) and the equilibrium free volume v_{fe} were defined in Chapter II as functions of temperature only. More generally, these quantities are functions of both temperature and pressure. Therefore, to accompany the concept of an equilibrium glass transition temperature T_{ge}, there must also be an equilibrium glass transition pressure P_{ge}. Throughout the following discussion, the phrase "above the transition" will mean on the rubbery side of the transition, and the phrase "below the transition" will mean on the glassy side of the transition. As before, taking $P_o v_o T_o$ to be an equilibrium state above the transition, the equations for the equilibrium volume are:

above the transition

$$\begin{aligned} v_e &= v_r \\ &= v_o - \alpha_r(T_o - T)v_o + \kappa_r(P_o - P)v_o \end{aligned} \qquad \text{(IV-4)}$$

below the transition

$$\begin{aligned} v_e &= v_g \\ &= v_o - \alpha_r(T_o - T_{ge})v_o - \alpha_g(T_{ge} - T)v_o \\ &\quad + \kappa_r(P_o - P_{ge})v_o + \kappa_g(P_{ge} - P)v_o \end{aligned} \qquad \text{(IV-5)}$$

above the transition

$$\begin{aligned} v_{fe} &= v_r - v_g \\ &= v_o\Delta\alpha(T - T_{ge}) - v_o\Delta\kappa(P - P_{ge}) \end{aligned} \qquad \text{(IV-6)}$$

below the transition

$$v_{fe} = 0 \tag{IV-7}$$

where

$$\Delta\alpha = \alpha_r - \alpha_g \tag{IV-8}$$

and

$$\Delta\kappa = \kappa_r - \kappa_g \tag{IV-9}$$

and κ is the compressibility. If $P_o v_o T_o$ were below the transition the equations for the equilibrium volume would be altered; however, the generality of equation (IV-1) would be unaffected.

As discussed previously, if only volume changes are occurring $c_{ij}^{-1*} = 0$. Therefore, if the stress has always been isotropic, equation (IV-1) reduces to

$$\int_{-\infty}^{t} \lambda^*(t') \frac{d}{dt'} [v_e(t') - v(t')]dt'$$
$$= \int_{-\infty}^{t} \lambda^*(t') \exp\left[- \int_{t'}^{t} \frac{dt''}{\tau(t'')} \right] \frac{dv_{fe}(t')}{dt'} dt' \quad . \tag{IV-10}$$

The following physical interpretation of equation (IV-10) is offered. If the term on the right were absent the solution to equation (IV-10) would be $v = v_e$; i.e., the volume would always "track" the equilibrium volume. Therefore, the term on the right may be thought of as producing the nonequilibrium effects. Physically, the factor $\exp[- \int_{t'}^{t} dt''/\tau(t'')]dv_{fe}(t')/dt'$ may be considered to be the potential for free volume change (i.e., it involves the temperature and/or pressure changes which might cause the free volume to change).

Whether or not the free volume change actually occurs depends upon the rate of temperature change and/or the rate of pressure change, relative to the relaxation time in the memory function. Above the transition, from equation (IV-6),

$$\frac{dv_{fe}(t')}{dt'} = v_o \Delta\alpha \frac{dT(t')}{dt'} - v_o \Delta\kappa \frac{dP(t')}{dt'} \qquad \text{(IV-11)}$$

and, thus, equation (IV-10) may be explicitly written in terms of rates of temperature and pressure changes. Therefore, above the transition, if either the relaxation time or the rates of temperature and pressure changes approach zero, the solution to equation (IV-10) is

$$v = v_e = v_r \qquad \text{(IV-12)}$$

and hence the volume follows the rubbery equilibrium line. This result is to be expected for very slow temperature and pressure changes, or, at very high temperatures, where the relaxation time is small. On the other hand, if $\tau \to \infty$, equation (IV-10) gives,

$$\int_{-\infty}^{t} \lambda^*(t') \frac{d}{dt'} [v_r(t') - v(t') - v_{fe}(t')dt' = 0 \qquad \text{(IV-13)}$$

from which the solution is seen to be

$$v = v_g + v_{fe}(-\infty) \tag{IV-14}$$

where $v_{fe}(-\infty)$ is the free volume which was present at $t' = -\infty$. Consequently, for large relaxation times, glassy-like behavior is predicted.

B. SPECIAL CASES OF THE GENERAL MODEL

The motivation for the specific form of equation (IV-1) is the manner in which it reduces in several special cases. These cases include: (1) reducing to incompressible viscoelastic theory if compressible effects are ignored, (2) reducing to linear elasticity for an equilibrium solid, and (3) reducing to a physically plausible volume rate equation under certain circumstances. These various special cases will now be discussed.

Reduction to Incompressible Viscoelastic Theory

If the condition of incompressibility is imposed then the volume changes will be zero and $\lambda^* \to \infty$; in this case the product $\lambda^* \frac{d}{dt'}\left[\frac{v_e(t') - v(t')}{v_o}\right]$ becomes indeterminate. Equation (IV-1) may then be written in the form of (II-23), where p represents the indeterminate scalar.

Reduction to Linear Elasticity

In this section it is shown how equation (IV-1) reduces to linear elasticity. For small strains c_{ij}^{-1} may be linearized to give (6)

$$c_{ij}^{-1} - \delta_{ij} = 2\tilde{\varepsilon}_{ij} \quad . \tag{IV-15}$$

Furthermore, taking the relaxation times to be large and the material parameters to be constant, and noting that $v_{fe} = 0$ for an equilibrium solid, equation (IV-1) may be written as

$$\sigma_{ij} + P\delta_{ij} + \lambda^*\left(\frac{v_e - v}{v_o}\right)\delta_{ij} = G\left(2\tilde{\varepsilon}_{ij} - \frac{2}{3}\,\frac{v - v_o}{v_o}\,\delta_{ij}\right) . \tag{IV-16}$$

For an equilibrium solid $P_o v_o T_o$ is below the transition and the equilibrium volume is given by

$$v_e = v_o - \alpha_g(T_o - T)v_o + \kappa_g(P_o - P)v_o \quad . \tag{IV-17}$$

Substituting equations (IV-2) and (IV-17) into equation (IV-16) and noting that the compressibility is the inverse of the bulk modulus gives

$$\sigma_{ij} + P_o\delta_{ij} = [\lambda \frac{v - v_o}{v_o} - \alpha_g(\lambda + \frac{2}{3} G)(T - T_o)]\delta_{ij} + 2G\tilde{\varepsilon}_{ij} \qquad \text{(IV-18)}$$

which is equivalent to equation (II-10) if the base state pressure P_o is taken as zero.

Reduction to a Volume Rate Equation

In this section it is shown how a rate equation may be obtained as a special case of equation (IV-1). As before, the equilibrium state $P_o v_o T_o$ is taken to be above the transition and the stress is presumed to have always been isotropic. In order to reduce equation (IV-1) to a rate equation, it is necessary to take the modulus λ^* to be constant. Under these circumstances equation (IV-1) gives

$$v_e(t) - v(t) = \int_{-\infty}^{t} \exp[- \int_{t'}^{t} \frac{dt''}{\tau(t'')}] \frac{dv_{fe}(t')}{dt'} dt' \quad . \qquad \text{(IV-19)}$$

Above the transition equation (IV-19) may be written

$$v_r(t) - v(t) = \int_{-\infty}^{t} \exp[- \int_{t'}^{t} \frac{dt''}{\tau(t'')}] \frac{dv_{fe}(t')}{dt'} dt' \quad . \qquad \text{(IV-20)}$$

Equation (IV-20) may be differentiated with respect to t using Leibnitz's rule; this differentiation gives

$$\frac{d}{dt}\,(v_r(t) - v(t)) = \frac{d}{dt}\int_{-\infty}^{t} \exp\Big[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\Big]\frac{dv_{fe}(t')}{dt'}\,dt'$$

$$= \int_{-\infty}^{t}\frac{\partial}{\partial t}\Big[\exp\Big[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\Big]\frac{dv_{fe}(t')}{dt'}\Big]dt'$$

$$+ \exp\Big[-\int_{t}^{t}\frac{dt''}{\tau(t'')}\Big]\Big[\frac{dv_{fe}(t')}{dt'}\Big]_{|t'=t}\Big(\frac{dt}{dt}\Big)$$

$$- \exp\Big[-\int_{-\infty}^{t}\frac{dt''}{\tau(t'')}\Big]\Big[\frac{dv_{fe}(t')}{dt'}\Big]_{|t'=-\infty}\Big(\frac{d(-\infty)}{dt}\Big)$$

$$= -\int_{-\infty}^{t}\exp\Big[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\Big]\frac{dv_{fe}(t')}{dt'}\frac{\partial}{\partial t}\Big[\int_{t'}^{t}\frac{dt''}{\tau(t'')}\Big]dt' + \frac{dv_{fe}(t)}{dt}$$

$$= -\frac{1}{\tau(t)}\int_{-\infty}^{t}\exp\Big[-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\Big]\frac{dv_{fe}(t')}{dt'}\,dt' + \frac{dv_{fe}(t)}{dt}\quad . \tag{IV-21}$$

The integral in equation (IV-21) is eliminated with equation (IV-20) giving

$$\frac{d}{dt}\,[v_r(t) - v(t)] = -\frac{v_r(t) - v(t)}{\tau(t)} + \frac{dv_{fe}(t)}{dt}\quad . \tag{IV-22}$$

Since $v_{fe} = v_r - v_g$ equation (IV-22) may be written

$$\frac{d}{dt}\,(v - v_g) = -\frac{v - v_r}{\tau}\quad . \tag{IV-23}$$

Below the transition equation (IV-19) gives

$$v_g(t) - v(t) = \int_{-\infty}^{t_{ge}} \exp\left[- \int_{t'}^{t} \frac{dt''}{\tau(t'')} \right] \frac{dv_{fe}(t')}{dt'} dt' \quad . \qquad \text{(IV-24)}$$

Equation (IV-24) may be differentiated as before to yield

$$\frac{d}{dt} (v - v_g) = - \frac{v - v_g}{\tau} \quad . \qquad \text{(IV-25)}$$

At constant pressure equation (IV-5) gives

$$\frac{dv_g}{dt} = \alpha_g \frac{dT}{dt} v_o = - \alpha_g R v_o \qquad \text{(IV-26)}$$

and therefore equation (IV-23) and equation (IV-25) may be summarized by (at constant pressure)

$$\frac{dv}{dt} = - \frac{v - v_e}{\tau} - \alpha_g R v_o \quad . \qquad \text{(IV-27)}$$

Equation (IV-27) is essentially equivalent to one of the rate equations stated by Kovacs (73,75) (see equation (II-29)). Two minor differences are worth noting. First, the cooling rate term in the Kovacs model is written as $\alpha_g R v_\infty$ instead of $\alpha_g R v_o$ and therefore is not constant during cooling. Secondly, the notation used by Kovacs implies that his rate equations are applicable only above the transition.

Equation (IV-27) may be stated in terms of temperature by dividing by R

$$\frac{dv}{dT} = \frac{v - v_e}{R\tau} + \alpha_g v_o \quad . \tag{IV-28}$$

For large cooling rates or relaxation times the solution to equation (IV-28) is

$$v = v_g + v_{fe}(0) \tag{IV-29}$$

where $v_{fe}(0)$ denotes the free volume which was present initially. Thus for fast cooling or at low temperatures, where the relaxation time is large, glassy behavior is predicted and all of the free volume present initially is frozen into the material.

CHAPTER V

ANALYSIS OF TIME DEPENDENT VOLUME CHANGES

In this chapter an analysis of the time dependent volume problem is presented. The necessary theoretical development is presented first, followed by the theoretical fits of the experimental data.

A. THEORETICAL ANALYSIS

The analysis of the volume problem begins with the rate equation derived in Chapter IV

$$\frac{dv}{dt} = - \frac{v - v_e}{\tau} - \alpha_g R v_o \quad . \qquad (V-1)$$

Inspection of equation (V-1) reveals that two important problems must be considered before the equation may be applied. These are: (1) the placement of the equilibrium lines v_r and v_g, and (2) determination of the functional form to use for τ .

The Equilibrium Lines

The placement of the equilibrium lines v_r and v_g requires numerical values for the coefficients of expansion α_r and α_g. Richardson and Savill (98) have reported that for polystyrene these quantities are approximately $\alpha_r = 6.00 \times 10^{-4}\ °C^{-1}$ and $\alpha_g = 2.25 \times 10^{-4}\ °C^{-1}$. However, both Kovacs (77) and Rusch (54) found it

necessary to take $\Delta\alpha$ to be temperature dependent in order to fit experimental data; also, in the present work it was found that the experimental data could not be fit using the above values for α_r and α_g. Therefore there seems to be substantial evidence indicating that the coefficients of expansion are temperature dependent; however, taking α_r and α_g to be functions of temperature introduces considerable mathematical difficulties. To avoid these difficulties, the equilibrium volume-temperature curve, resulting from a temperature dependent coefficient of expansion, may be approximated by a series of straight lines as shown in Figure 8. At high and low temperatures the coefficients of expansion listed above were used; in the intermediate temperature range the values used were $\alpha_g = 2.72 \times 10^{-4}\ °C^{-1}$ and $\alpha_r = 3.70 \times 10^{-4}\ °C^{-1}$, as shown in Figure 8. There is some arbitrariness in the placement of the intermediate lines and thus α_r and α_g may be considered semi-adjustable parameters. The intermediate values listed above were used to fit all of the volume data in this work.

The Relaxation Time and Shift Factors

The functional form used for τ is probably the most crucial aspect of the volume problem. As discussed in Chapter II, τ is usually taken to be dependent on both temperature and free volume. Two such functions were presented in Chapter II; these equations were due to Rusch (54) and to Kovacs (77). The two forms are similar in that the effective relaxation time τ is obtained by multiplying a single reference relaxation time τ_r by a shift factor.

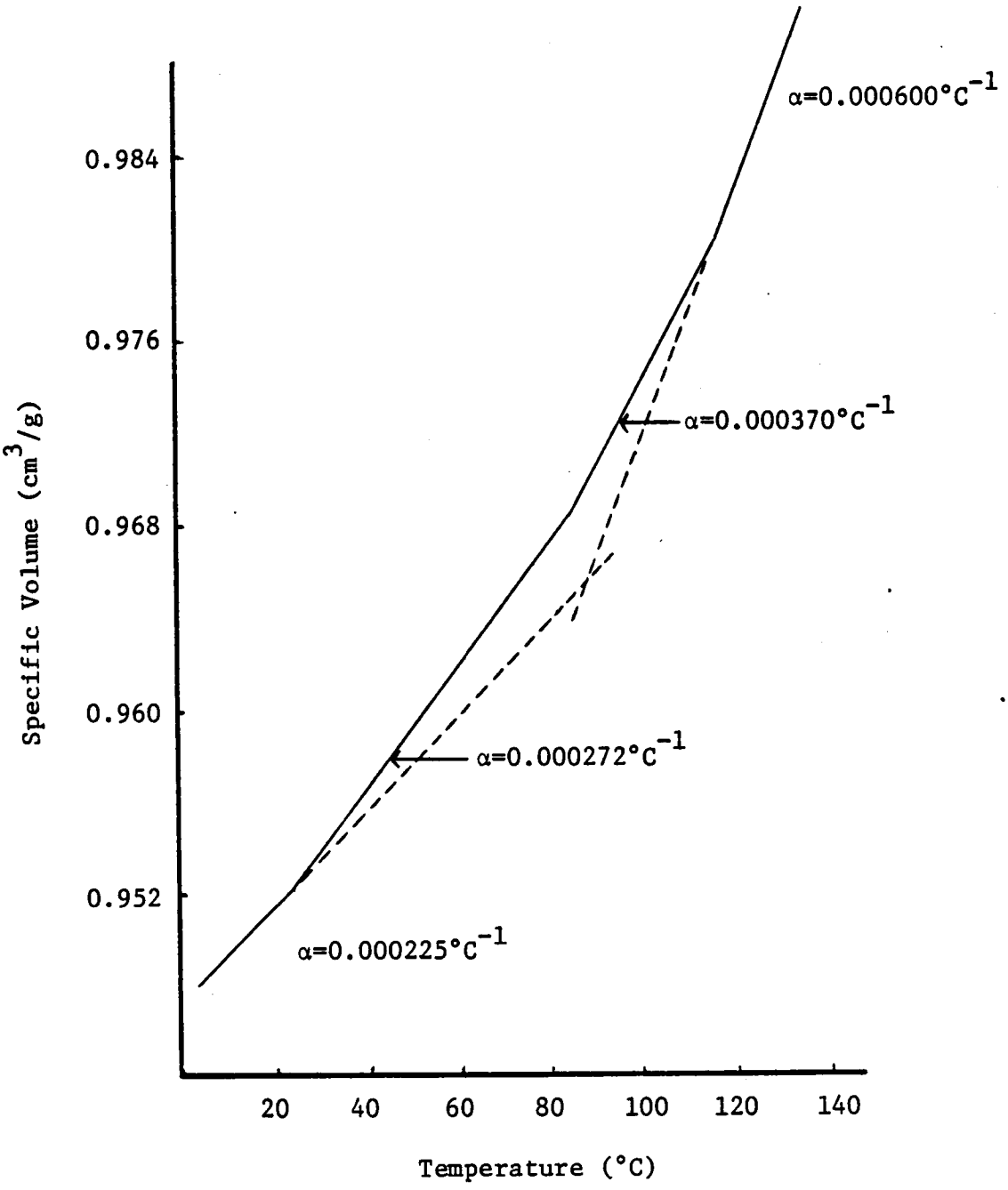


Figure 8. Placement of the rubbery and glassy equilibrium lines.

Thus in both cases a single relaxation time is shifted over the entire temperature range of interest. The same procedure was attempted in the present research, but was found to be inadequate, at least if the shift factor had the normal exponential dependence on temperature and free volume. The mathematical problem is to determine the functional form for τ such that the proper behavior is exhibited at both high and low temperatures. At high temperatures the relaxation time should exhibit a WLF equation type of temperature dependence; however, at lower temperatures the relaxation time cannot become so large so as to prevent volume aging.

It seems physically reasonable to postulate that at high temperatures the effective relaxation time approaches a characteristic rubbery asymptote, while at lower temperatures the effective relaxation time tends to a glassy asymptote. Furthermore, the rubbery component should primarily depend on the temperature and the glassy component should primarily be a function of free volume. An equation which has the proper characteristics at high and low temperatures is

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_G} \tag{V-2}$$

or

$$\tau = \frac{\tau_R \tau_G}{\tau_R + \tau_G} \tag{V-3}$$

where τ_R and τ_G are the rubbery and glassy components of the effective relaxation time. At high temperatures $\tau_G >> \tau_R$ and thus

$\tau \cong \tau_R$; at lower temperatures $\tau_R >> \tau_G$ which gives $\tau \cong \tau_G$. The functions τ_R and τ_G are shifted from the reference temperature with equations modeled after Kovacs (77)

$$\tau_R = \tau_{rR} a_{TR} a_{VR} \tag{V-4}$$

and

$$\tau_G = \tau_{rG} a_{TG} a_{VG} \tag{V-5}$$

where τ_{rR} and τ_{rG} denote the values of the rubbery and glassy relaxation times at the reference temperature. The quantities a_{TR}, a_{VR}, a_{TG}, and a_{VG} are the shift factors; their specific forms will be presented later. To simplify the equations somewhat, and to reduce the number of parameters that must be determined, it is convenient to take

$$\tau_{rR} = \tau_{rG} = \tau_r \tag{V-6}$$

and

$$a_{VR} = a_{VG} = a_V \quad . \tag{V-7}$$

The effective relaxation time, given by equation (V-3), may now be written

$$\tau = \tau_r \left(\frac{a_{TR} a_{TG}}{a_{TR} + a_{TG}} \right) a_V \quad . \tag{V-8}$$

For convenience, the reference temperature is chosen as the equilibrium glass transition temperature, T_{ge}. The equations for the shift factors may now be written

$$a_{TR} = \begin{cases} \exp\left[\frac{C_1}{T - C_2} (T_{ge} - T)\right]; T > T_{ge} \\ \exp\left[\frac{C_1}{T_{ge} - C_2} (T_{ge} - T)\right]; T < T_{ge} \end{cases} \qquad \text{(V-9)}$$

$$a_{TG} = \exp[C_T(T_{ge} - T)] \qquad \text{(V-10)}$$

$$a_V = \exp\left[- C_V \frac{v_{fn} - w_{fc}}{v_f} \right] . \qquad \text{(V-11)}$$

The quantities C_1, C_2, C_T, C_V, and w_{fc} will be discussed later. The forms of the temperature dependent shift factors (a_{TR} and a_{TG}) are the same as those used by Kovacs (77) (see equation (II-34)). The a_V equation is motivated by the Kovacs form (see equation (II-35)), although there are some differences between the two. The two most noteworthy differences are: (1) Kovacs' equation does not include the free volume in the denominator as equation (V-11) does, and (2) equation (V-11) includes an empirically introduced adjustable parameter, w_{fc}, which is absent from the Kovacs shift factor.

A plot of the temperature dependence of the relaxation time is shown in Figure 9. The plot shows the temperature dependence of the effective relaxation time τ, the rubbery and glassy relaxation times τ_R and τ_G, and the WLF relaxation time τ_{WLF}. Note that at high

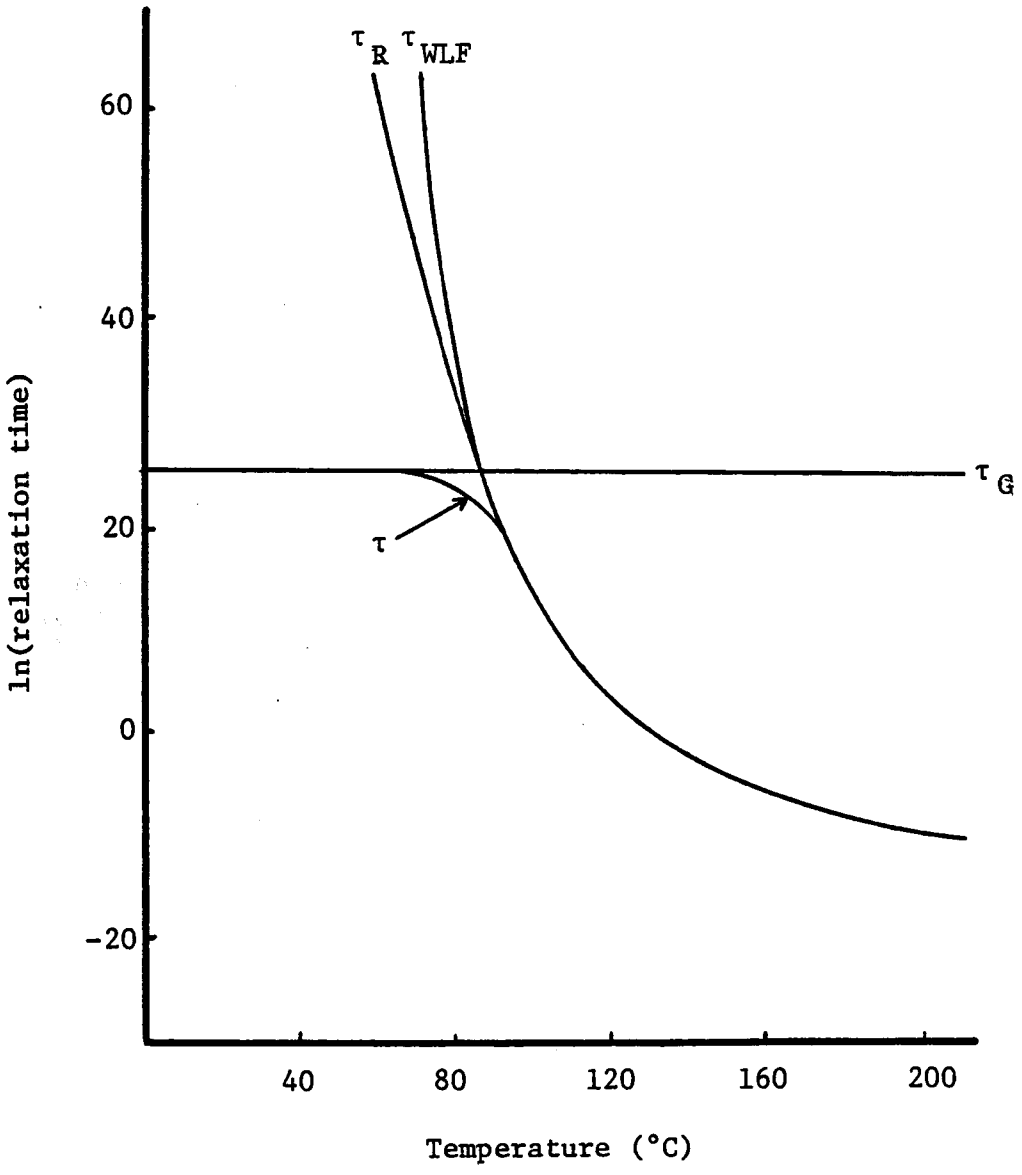


Figure 9. Temperature dependence of the relaxation time.

temperatures $\tau = \tau_R = \tau_{WLF}$ and at low temperatures $\tau = \tau_G$. The numerical values of the constants are $C_1 = 45.03$, $C_2 = 59.03°C$, $T_{ge} = 85.0°C$, $C_T = 10^{-4}\ °C^{-1}$ and $\tau_r = 7.2 \times 10^{10}$ sec, which is the relaxation time at 85°C. The values of τ_r, C_1, and C_2 were selected so as to obtain WLF equation behavior at high temperatures. The small value of C_T was chosen to essentially eliminate the temperature dependence of the glassy relaxation time.

Figure 10 shows a plot of the nonequilibrium free volume dependence of the relaxation time. Two curves are shown in Figure 10; the value of C_V is 15.0 in both cases. These plots also require a numerical value for w_{fc} which was introduced as an empirical adjustable parameter. The curves illustrate the effects of w_{fc}, and also of the equilibrium free volume v_{fe}, on the shift factor. Equation (V-11) shows that, at temperatures less than T_{ge}, the shift factor becomes infinite as the free volume approaches zero (since $w_{fc} > 0$). This behavior is exemplified by the lower curve ($w_{fc} = 0.001$, $v_{fe} = 0.0$) in Figure 10. The numerical value of C_V is essentially the same as the corresponding parameter used by Kovacs (77). To fit aging data it was necessary to take C_V to be somewhat temperature dependent; it was taken to be 15.0 during cooling and during aging at 90°C and 70°C; it was decreased to 12.5 to fit the 25°C aging data. Kovacs (77) also indicated that the corresponding parameter was a function of temperature.

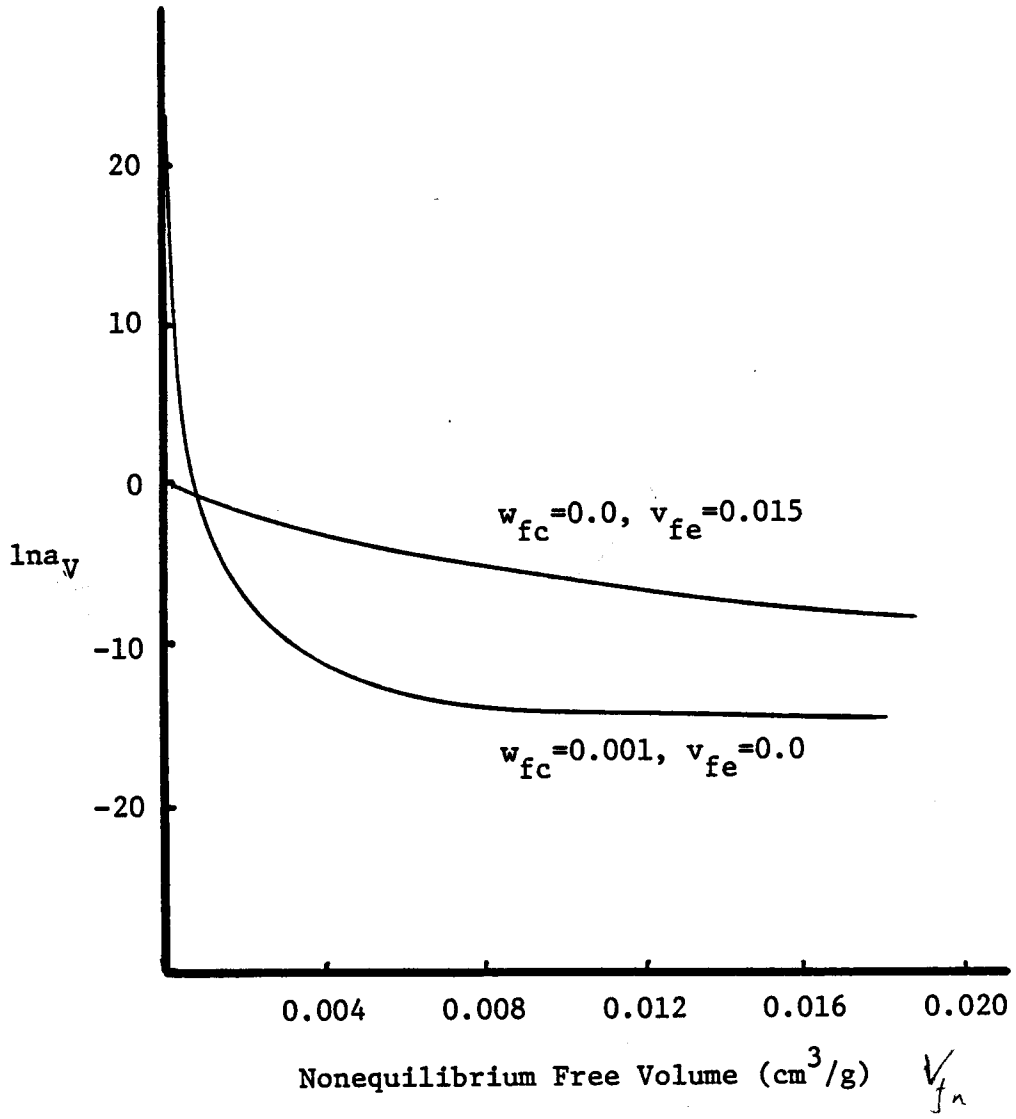


Figure 10. Nonequilibrium free volume dependence of the relaxation time.

B. FITTING THE EXPERIMENTAL DATA

In this section the theoretical fits of the experimental data are presented. The numerical values of most of the parameters used to fit the data were given in the prior section; obviously there are many parameters to be determined. For clarity all of the numerical values used for the various parameters are collected together in Table I. These parameters are classified in two categories: (1) those whose values can be reasonably justified from prior work in the literature (semi-adjustable parameters), and (2) those which were explicitly introduced in the present work (fully adjustable parameters).

Cooling Curves

Using the equations of the previous section and the numerical values in Table I, the rate equation may be used to generate volume-temperature curves during cooling. Equation (V-1) was solved numerically using Euler's method. The computer program is listed in Appendix B. Figure 11 shows two cooling curves obtained at cooling rates of 0.010°C/sec and 160°C/sec. The linear portion of the volume curve, parallel to the glassy equilibrium line, may be extrapolated to higher temperatures until it intersects the rubbery equilibrium line; the intersection point is the apparent glass transition temperature. The extrapolations are not shown in Figure 11, but the extrapolated values of T_g are given. These volume-temperature curves may be obtained for a variety of cooling rates; the extrapolations

TABLE I

SUMMARY OF PARAMETERS USED IN VOLUME STUDIES

Semi-adjustable parameters (values in reasonable agreement with prior literature):

v_o = 0.980 cm^3/g (at T_o = 118°C)

α_r = 0.000370°C^{-1}

α_g = 0.000272°C^{-1}

τ_r = 7.2 x 10^{10} sec

T_{ge} = 85°C

C_1 = 45.03

C_2 = 59.03°C

C_V = 15.0 (during cooling, 90°C aging, 70°C aging)

C_V = 12.5 (25°C aging)

Fully adjustable parameters (values determined empirically in the present work):

C_T = 1.0 x 10^{-4} °C^{-1}

w_{fc} = 0.0 (during cooling)

w_{fc} = 0.00080 cm^3/g (90°C aging)

w_{fc} = 0.00020 cm^3/g (70°C aging, 25°C aging)

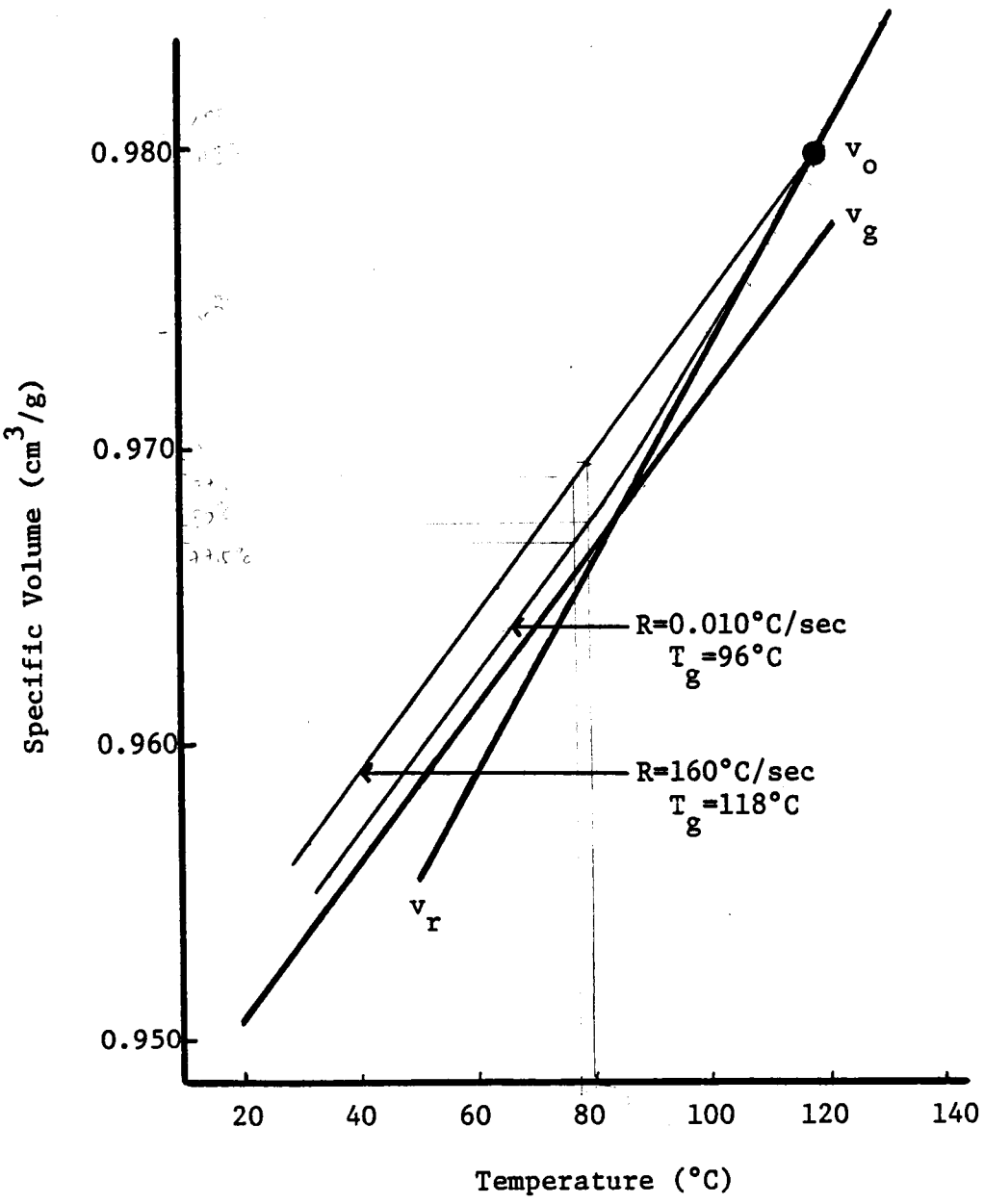


Figure 11. Cooling curves and extrapolated values of T_g.

then give the approximate dependence of T_g on the cooling rate. Figure 12 shows the theoretical cooling rate dependence of T_g obtained using the above procedure up to cooling rates of about 5°C/sec. The experimental data in Figure 12 were obtained by Wust (96). While there is considerable scatter at cooling rates greater than about 1°C/sec, the data are believed to be reliable up to about 1°C/sec. At these low cooling rates the theoretical curve has the correct general shape although it underpredicts T_g by a few degrees.

Aging Curves

Aging curves were obtained by numerically solving equation (V-1) with the cooling rate set equal to zero. Again Euler's method was employed. The computer program is listed in Appendix B. The numerical values of the parameters are shown in Table I. Figures 13, 14, and 15 show theoretical fits of the data. The theoretical curves at 25°C and 70°C are quite acceptable; the value used for the adjustable parameter w_{fc} was taken as 0.00020 in both cases. Using this same value of w_{fc} at 90°C, however, does not give an acceptable fit of the data. Using $w_{fc} = 0.00020$ at 90°C produces an aging curve which overestimates the density; the curve climbs quickly (as it should) but does not become flat until $(\rho - \rho_o)/\rho_o \cong 20 \times 10^{-4}$. In order to obtain the curve shown in Figure 15, it was necessary to take $w_{fc} = 0.00080$. One of the problems at 90°C may be the placement of the equilibrium lines; as the temperature approaches T_g this becomes more difficult. Also, as noted in Chapter III, the reliability

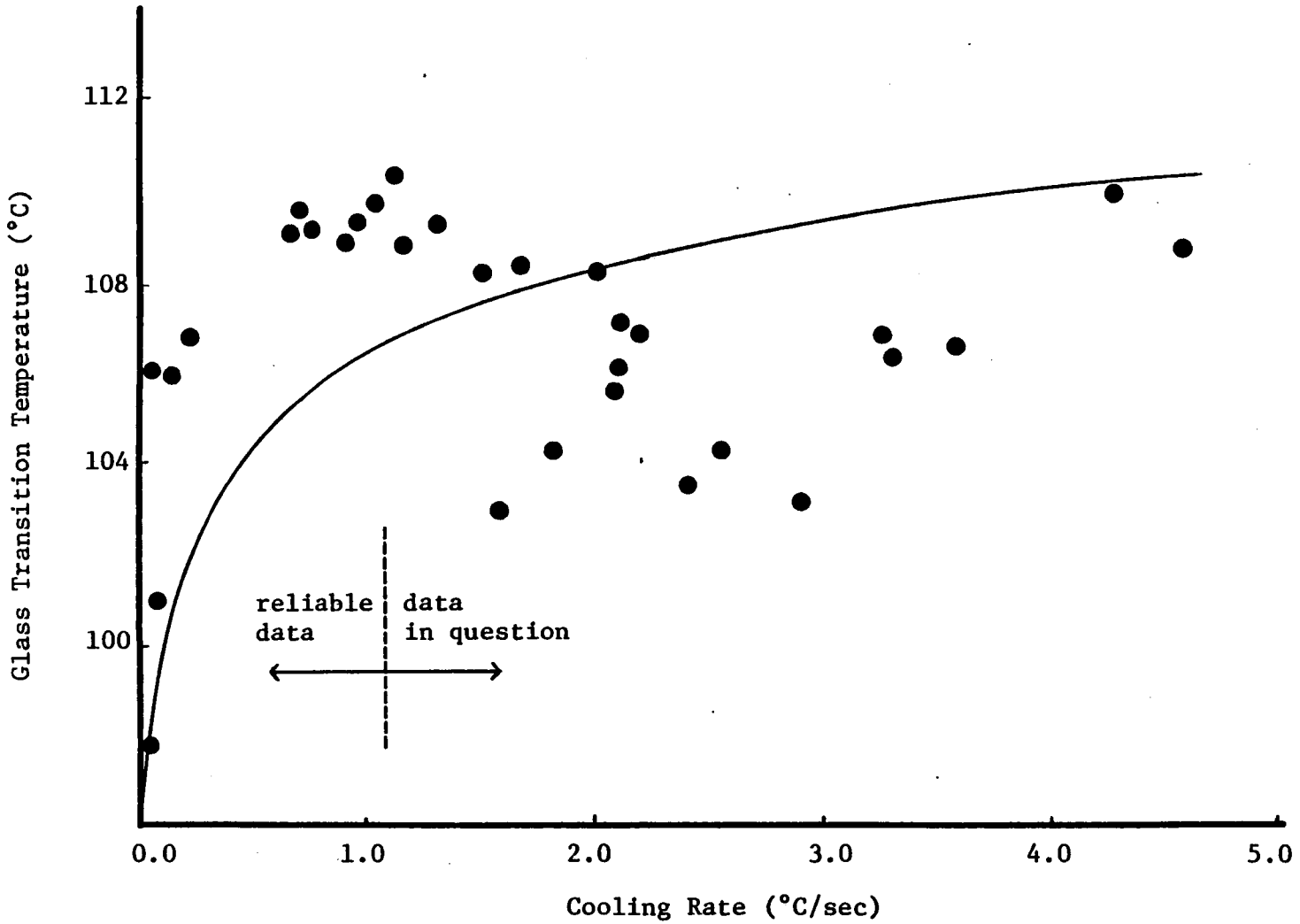


Figure 12. Theoretical fit of the cooling rate dependence of T_g.

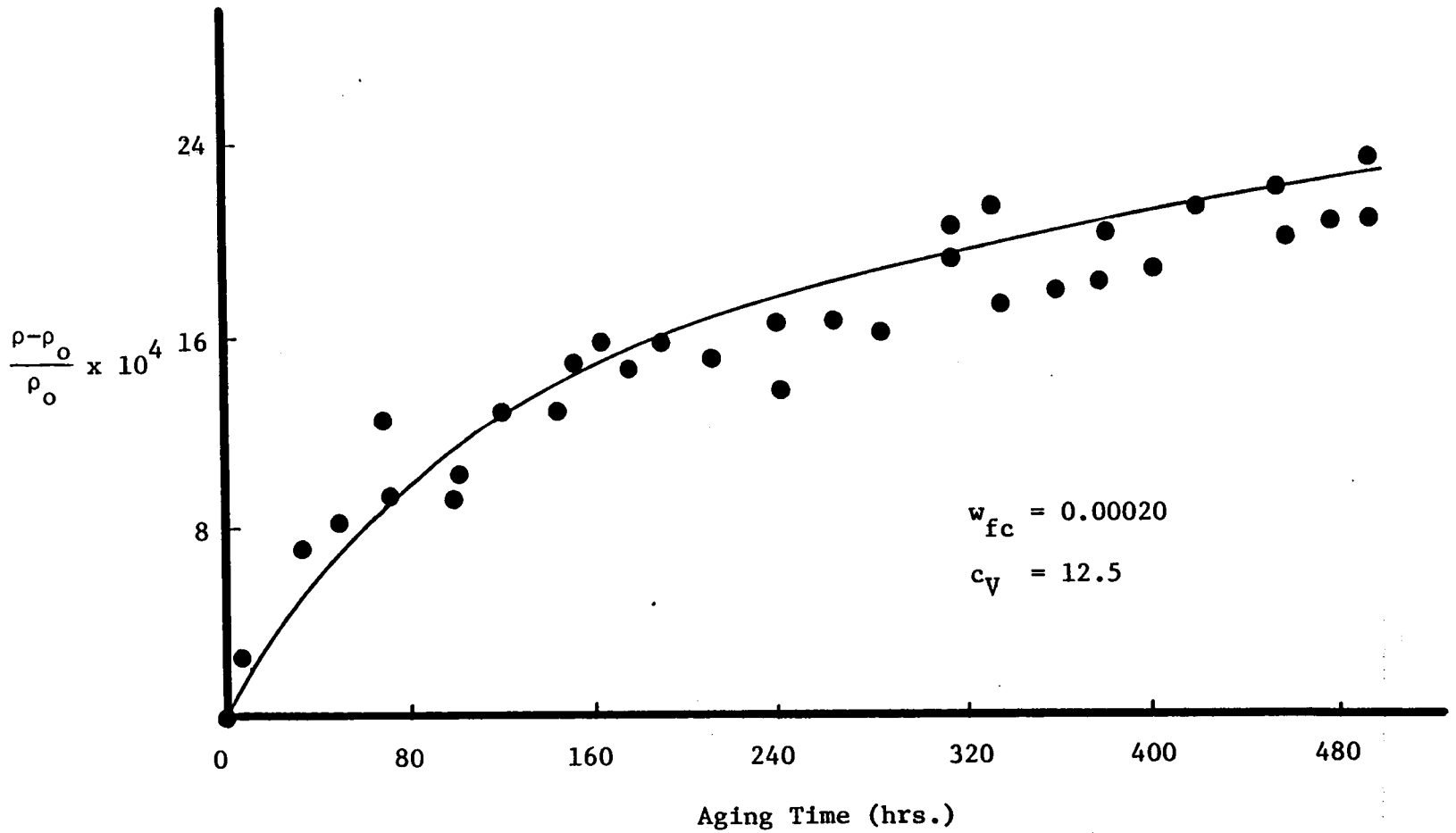


Figure 13. Theoretical fit of 25°C aging data.

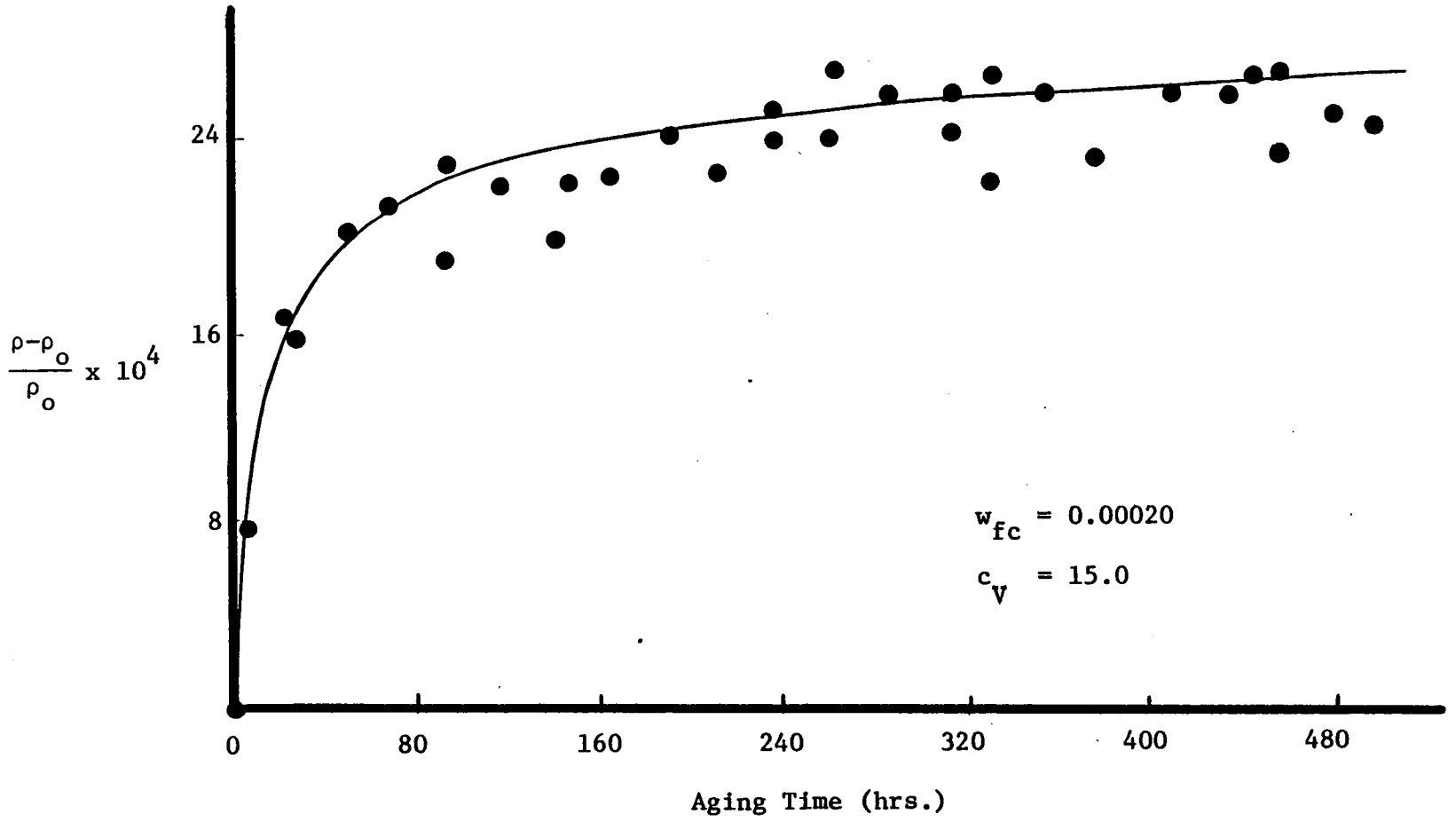


Figure 14. Theoretical fit of 70°C aging data.

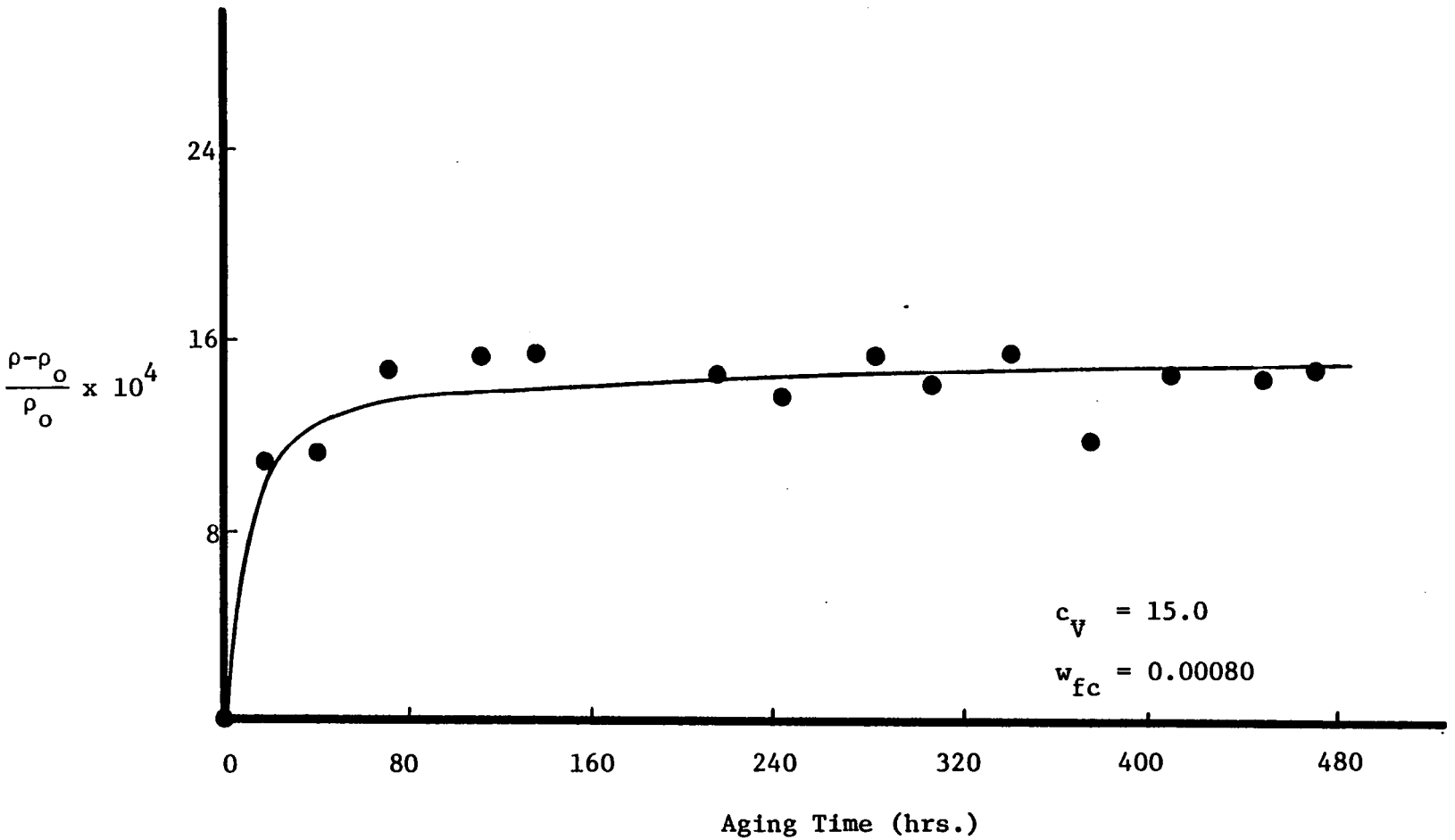


Figure 15. Theoretical fit of 90°C aging data.

of the data begins to be questionable at temperatures near 90°C because of the assumed relationship between the measured density and the aging density.

CHAPTER VI

ANALYSIS OF SHRINKAGE (ORIENTATION AGING) PROBLEM

In this chapter an analysis of orientation aging in polystyrene at temperatures below T_g is presented. The experimental data which will be considered were obtained by Potnis (95) (see Chapter II); his procedure will be summarized later in this chapter. The first part of the chapter is concerned with the necessary theoretical development; the second part of the chapter deals with fitting the experimental data.

A. THEORETICAL ANALYSIS

The problem considered in this chapter falls into the broad category of determining elastic recovery in a viscoelastic material. Physically such problems involve subjecting the material to a deformation after which the stress is released; the material may exhibit a partial recovery. No attempt is made here to review the literature concerning elastic recovery in viscoelastic materials; for a review of the pertinent literature and for a general treatment of elastic recovery the reader is referred to a paper by White (35). An important point is worth noting at this time. If a Maxwell type model is used for the elastic recovery calculations, and only one term is present in the memory function, then no delayed recovery is predicted; that is, when the stress is released there is an instantaneous

deformation, but no further deformation (1,35,99). Therefore, if delayed recovery is desired, the memory function must include at least two terms.

General Model and Kinematics

Before discussing the theoretical synthesis of the problem, it is first desirable to briefly describe the experimental procedure. The experiments were performed by Potnis and complete details are available in his thesis (95). Cylindrically shaped samples of polystyrene, about 0.5 mm in diameter, were pulled in an Instron tensile tester at 105°C. The initial length of the samples was about 4.0 cm and they were pulled to five times their initial length at a crosshead speed of 1000 mm/min. Following the deformation the samples were quickly cooled (through an air quench) to room temperature after which the Instron clamps were released. This procedure produced highly oriented glassy samples. The decay of the orientation (orientation aging) in these samples, under various loadings, was then monitored at 90°C, 80°C, and 70°C. The specific loads will be discussed later. The degree of orientation decay was determined by measuring both the birefringence and the shrinkage of the samples. Potnis considered the correlation between the rate of birefringence decay and the rate of shrinkage; details are available in his thesis (95). In this work only the shrinkage data is of concern.

Physically, the experimental procedure may be thought of as a rubbery pulling at a temperature just above T_g. The deformation is rapid and the molecules become oriented; before the orientation has

time to decay the sample is cooled through T_g and the orientation is frozen into the sample. After cooling, the Instron clamps are released and the stress instantaneously becomes zero; there must also be an instantaneous deformation when the stress is released. However, because the material is glassy-like after being cooled, there is the physical picture of a large glassy modulus accompanying a small instantaneous deformation to balance the stress which was instantly released.

Compressible effects will not be considered in this analysis; consequently the appropriate form of the nonisothermal viscoelastic model is

$$\sigma_{ij} = - p\delta_{ij} + \int_{-\infty}^{t} m_1(t,t')c_{ij}^{-1}(t,t')dt' \qquad \text{(VI-1)}$$

where

$$m_1(t,t') = \sum_n \frac{G_n(t')}{\tau_n(t')} \exp\left[-\int_{t'}^{t} \frac{dt''}{\tau_n(t'')} \right] . \qquad \text{(VI-2)}$$

The "1" direction is defined as the pulling direction; using $\sigma_{22} = 0$, equation (VI-1) gives

$$\sigma_{11} = \int_{-\infty}^{t} m_1(t,t')[c_{11}^{-1}(t,t') - c_{22}^{-1}(t,t')]dt' . \qquad \text{(VI-3)}$$

The deformation rate $\dot{E}$, defined by

$$\dot{E} = \frac{1}{L} \frac{dL}{dt} \qquad \text{(VI-4)}$$

where L is the sample length, is not constant during Instron pulling. However, mathematical simplifications are possible if an equivalent constant $\dot{E}$ is used. This value of $\dot{E}$ is selected so that the calculated strain after the deformation is correct. If L_r and L_g denote the length of the sample before and after the deformation, and if V_x is the crosshead speed, then the time of the deformation, t_d, is given by

$$t_d = \frac{L_g - L_r}{V_x} = \frac{(20.0 - 4.0)\ \text{cm}}{100.0\ \text{cm/min}} = 0.16\ \text{min} = 0.00267\ \text{hr}. \qquad \text{(VI-5)}$$

If $\dot{E}$ is constant, equation (VI-4) gives

$$L_g = L_r \exp(\dot{E} t_d) \quad . \qquad \text{(VI-6)}$$

The experimental strain after the deformation was $L_g/L_r = 5.0$, which shows that the appropriate equivalent $\dot{E}$ is 600 hr^{-1}. In addition to obtaining the correct strain after the deformation, it is also important that the experimental and calculated stresses be in agreement; this will be discussed later.

The mathematical problem is to solve for the length of the sample after the Instron clamps are released; the clamps are released at time $t' = 0$. An unknown deformation function, f(t), may be defined for $t > 0$ as

$$f(t) = \frac{L(t)}{L_g} \qquad \text{(VI-7)}$$

where L(t) denotes the length of the sample at any time $t > 0$. The tensile stress at any time $t > 0$ may be expressed in terms of the load on the sample and the cross-sectional area with the equation

$$\sigma_{11} = \frac{F}{A(t)} \tag{VI-8}$$

where F is the load on the sample and A(t) is the cross-sectional area. Assuming the material to be incompressible, equation (VI-8) may be written

$$\sigma_{11} = \frac{F}{A_g} \frac{L(t)}{L_g} = \sigma_o f(t) \tag{VI-9}$$

where A_g denotes the cross-sectional area at the end of the deformation and σ_o is defined by

$$\sigma_o = \frac{F}{A_g} \quad . \tag{VI-10}$$

The diameter of the samples after the deformation was about 0.25 mm; this gives a numerical value for σ_o of

$$\sigma_o = (2.0 \times 10^6)m \text{ dynes/cm}^2 \tag{VI-11}$$

where m is the mass in grams which was suspended from the sample. Three loads were investigated: (1) $m = 0$, $\sigma_o = 0$; (2) $m = 1$ g, $\sigma_o = 2.0 \times 10^6$ dynes/cm^2; (3) $m = 10$ g, $\sigma_o = 2.0 \times 10^7$ dynes/cm^2.

It may now be noted that for $t > 0$ equation (VI-3) may be written

$$\sigma_{11} = \sigma_o f(t) = \int_{-\infty}^{t} m_1(t,t')[c_{11}^{-1}(t,t') - c_{22}^{-1}(t,t')]dt' \quad . \tag{VI-12}$$

The kinematical description of the problem for $t > 0$ is now considered. The components of the Finger strain tensor are given by

$$c_{ij}^{-1} = \frac{\partial x_i}{\partial X_k} \frac{\partial x_j}{\partial X_k} \tag{VI-13}$$

where x denotes a coordinate at time t (the present time) and X denotes a coordinate at time t' (past time). The restriction of incompressibility gives

$$\det|c_{ij}^{-1}| = 1 \quad . \tag{VI-14}$$

which, for this problem, reduces to

$$c_{22}^{-1} = c_{33}^{-1} = [1/c_{11}^{-1}]^{1/2} \quad . \tag{VI-15}$$

At 105°C (the deformation temperature) the relaxation time and the modulus are denoted by τ_p and G_p; at the aging temperature (90°C, 80°C, or 70°C) these quantities are denoted by τ_s and G_s. During cooling τ and G change with time; however, for mathematical convenience the values of τ and G during the cooling step are taken equal to their values at the aging temperature (τ_s and G_s). The

time of cooling is denoted by t_c. Using the above nomenclature, the following kinematics are proposed for $t > 0$:

$-\infty < t' < -t_1$ [material at rest; 105°C]

$$\tau = \tau_p;\ G = G_p$$

$$c_{11}^{-1} = (f(t))^2 \exp(2\dot{E}t_d)$$

$$c_{22}^{-1} = (f(t))^{-1} \exp(-\dot{E}t_d) \qquad \text{(VI-16)}$$

$-t_1 < t' < -t_2$ [material is deformed; 105°C]

$$\tau = \tau_p;\ G = G_p;\ t_d = t_1 - t_2$$

$$c_{11}^{-1} = (f(t))^2 \exp[-2\dot{E}(t_2 + t')]$$

$$c_{22}^{-1} = (f(t))^{-1} \exp[\dot{E}(t_2 + t')] \qquad \text{(VI-17)}$$

$-t_2 < t' < 0$ [material is cooled]

$$\tau = \tau_s;\ G = G_s;\ t_c = t_2$$

$$c_{11}^{-1} = (f(t))^2$$

$$c_{22}^{-1} = (f(t))^{-1} \qquad \text{(VI-18)}$$

$0 < t' < t$ [unknown deformation at the aging temperature]

$$\tau = \tau_s;\ G = G_s$$

$$c_{11}^{-1} = (f(t)/f(t'))^2$$

$$c_{22}^{-1} = (f(t)/f(t'))^{-1} \quad . \tag{VI-19}$$

General Results and Limiting Cases

The kinematics in equations (VI-16) through (VI-19) and the memory function in equation (VI-2) may be substituted into equation (VI-12) to give

$$\sigma_o f(t) = \int_{-\infty}^{-t_1} \sum_n \frac{G_{np}}{\tau_{np}} \exp\left[-\int_{t'}^{-t_2} \frac{dt''}{\tau_{np}} - \int_{-t_2}^{t} \frac{dt''}{\tau_{ns}} \right]$$

$$x \left[(f(t))^2 \exp[2\dot{E}t_d] - (f(t))^{-1}\exp[-\dot{E}t_d]\right]dt'$$

$$+ \int_{-t_1}^{-t_2} \sum_n \frac{G_{np}}{\tau_{np}} \exp\left[-\int_{t'}^{-t_2} \frac{dt''}{\tau_{np}} - \int_{-t_2}^{t} \frac{dt''}{\tau_{ns}} \right]$$

$$x \left[(f(t))^2 \exp[-2\dot{E}(t_2 + t')]\right.$$

$$\left. - (f(t))^{-1}\exp[\dot{E}(t_2 + t')]\right]dt'$$

$$+ \int_{-t_2}^{0} \sum_n \frac{G_{ns}}{\tau_{ns}} \exp\left[-\int_{t'}^{t} \frac{dt''}{\tau_{ns}} \right]\left[(f(t))^2 - (f(t))^{-1}\right]dt'$$

$$+ \int_{0}^{t} \sum_n \frac{G_{ns}}{\tau_{ns}} \exp\left[-\int_{t'}^{t} \frac{dt''}{\tau_{ns}} \right]\left[\left(\frac{f(t)}{f(t')}\right)^2 - \left(\frac{f(t)}{f(t')}\right)^{-1}\right]dt' \quad . \tag{VI-20}$$

Since G_{np}, τ_{np}, G_{ns}, and τ_{ns} are constant all of the integrations in equation (VI-20), with the exception of the integral containing the

unknown function $f(t')$, may be performed. After considerable manipulation, equation (VI-20) may be put into the following form:

$$\sigma_o f(t) = \sum_n [A_n (f(t))^2 - B_n (f(t))^{-1}] \exp\left(- \frac{t}{\tau_{ns}} \right)$$

$$+ \sum_n C_n \left[(f(t))^2 \int_0^t (f(t'))^{-2} \exp\left(- \frac{t - t'}{\tau_{ns}} \right) dt' \right.$$

$$\left. - (f(t))^{-1} \int_0^t f(t') \exp\left(- \frac{t - t'}{\tau_{ns}} \right) dt' \right] \qquad \text{(VI-21)}$$

where the coefficients A_n, B_n, and C_n are given by

$$A_n = G_{np} \exp\left(- \frac{t_c}{\tau_{ns}} \right) \exp\left[- (1 - 2\dot{E}\tau_{np}) \frac{t_d}{\tau_{np}} \right]$$

$$+ \frac{G_{np}}{1 - 2\dot{E}\tau_{np}} \exp\left(- \frac{t_c}{\tau_{ns}} \right) \left[1 - \exp\left[- (1 - 2\dot{E}\tau_{np}) \frac{t_d}{\tau_{np}} \right] \right]$$

$$+ G_{ns} \left[1 - \exp\left(- \frac{t_c}{\tau_{ns}} \right) \right] \qquad \text{(VI-22)}$$

$$B_n = G_{np} \exp\left(- \frac{t_c}{\tau_{ns}} \right) \exp\left[- (1 + \dot{E}\tau_{np}) \frac{t_d}{\tau_{np}} \right]$$

$$+ \frac{G_{np}}{1 + \dot{E}\tau_{np}} \exp\left(- \frac{t_c}{\tau_{ns}} \right) \left[1 - \exp\left[- (1 + \dot{E}\tau_{np}) \frac{t_d}{\tau_{np}} \right] \right]$$

$$+ G_{ns} \left[1 - \exp\left(- \frac{t_c}{\tau_{ns}} \right) \right] \qquad \text{(VI-23)}$$

$$C_n = \frac{G_{ns}}{\tau_{ns}} \, . \qquad \text{(VI-24)}$$

The mathematical problem is to solve equation (VI-21) for the unknown function f(t). Clearly this requires a numerical scheme. However, before discussing the numerical solution, there are several special cases where the solution may be obtained analytically. All of the following special cases are restricted to $\sigma_o = 0$ (i.e. restricted to unloaded samples). The cases to be considered include: (1) the instantaneous deformation (t = 0), (2) a single term memory function ($G_n = 0(n > 1)$ or $\tau_n = \tau_{n+1}$), (3) the viscous limit ($\tau_p = 0$), and (4) the elastic limit ($\tau_p \to \infty$). At t = 0 equation (VI-21) gives

$$f_o = \left[\frac{\sum_n B_n}{\sum_n A_n} \right]^{1/3} \qquad \text{(VI-25)}$$

where f_o is the instantaneous deformation. If $G_n = 0(n > 1)$ equation (VI-21) reduces to

$$0 = A_1(f(t))^2 - B_1(f(t))^{-1} + C_1(f(t))^2 \int_0^t (f(t'))^{-2} \exp\left(\frac{t'}{\tau_{1s}}\right) dt' - C_1(f(t))^{-1} \int_0^t f(t') \exp\left(\frac{t'}{\tau_{1s}}\right) dt' \quad . \qquad \text{(VI-26)}$$

It is readily seen that $f(t) = f_o$ is the solution to equation (VI-26), and therefore no delayed recovery occurs if $G_n = 0(n > 1)$. This same result ($f(t) = f_o$) may be deduced for the case $\tau_n = \tau_{n+1}$. Both

of these cases ($G_n = 0(n > 1)$ and $\tau_n = \tau_{n+1}$) correspond to a one-term memory function and thus the instantaneous deformation is the only recovery possible. If $\tau_p = 0$ the coefficients A_n and B_n are equal

$$A_n = B_n = G_{np}\exp\left(-\frac{t_c}{\tau_{ns}}\right) + G_{ns}\left[1 - \exp\left(-\frac{t_c}{\tau_{ns}}\right)\right] \qquad \text{(VI-27)}$$

which gives $f_o = 1$; also, $f(t) = f_o = 1$ is the solution to equation (VI-21) if $A_n = B_n$, and therefore there is no instantaneous or delayed recovery if $\tau_p = 0$. Physically, this implies that the material instantly "forgets" its past history, and thus none of the strain is recoverable. If attention is restricted to isothermal deformation and recovery, and $\tau_{ns} = \tau_{np} \to \infty$ and $G_{ns} = G_{np}$, the coefficients A_n and B_n become

$$A_n = G_{np}\exp(2\dot{E}t_d) \qquad \text{(VI-28)}$$

$$B_n = G_{np}\exp(-\dot{E}t_d) \qquad \text{(VI-29)}$$

These equations give

$$f_o = \exp(-\dot{E}t_d) \qquad \text{(VI-30)}$$

and thus all of the strain is instantly recoverable; also $f(t) = f_o = \exp(-\dot{E}t_d)$ is the solution to equation (VI-21) if $\tau_{np} = \tau_{ns} \to \infty$ and therefore no delayed deformation occurs. Physically, $\tau \to \infty$ corresponds to the elastic asymptote in which the original rubbery

length L_r acts as a reference state to which the material instantly returns when the stress is released.

B. FITTING THE EXPERIMENTAL DATA

The theoretical delayed deformation is obtained by numerically solving equation (VI-21) for the unknown deformation function f(t). The integrals are evaluated using a trapezoidal rule. The solution of equation (VI-21) requires a trial and error stepping procedure; a successive approximation method was used. The computer program is listed in Appendix B.

As discussed previously, delayed deformation is not predicted if a single term memory function is used; therefore two terms are included in the memory function. The numerical values of the parameters employed are shown in Table II. The relaxation times τ_{1s} and τ_{2s} were both shifted with the same shift factor between 90°C and 70°C

$$\tau_{ns} = \tau_{rns} a_{To} \qquad \text{(VI-31)}$$

where τ_{rns} denotes the relaxation time at a reference temperature, T_r. The shift factor is given by

$$a_{To} = \exp[C_o(T_r - T)] \ . \qquad \text{(VI-32)}$$

For convenience the reference temperature is taken as 90°C; the

TABLE II

SUMMARY OF PARAMETERS USED IN THE ORIENTATION AGING PROBLEM

Temperature (°C)	Moduli (dynes/cm^2)		Relaxation Times (hours)	
	G_1	G_2	τ_1	τ_2
105	1.3×10^6	1.3×10^6	1.0	1.0
90	2.7×10^9	1.4×10^7	0.010	30
80	1.0×10^{10}	1.0×10^9	0.030	90
70	3.0×10^{10}	3.0×10^{10}	0.090	270

equivalent deformation rate = $\dot{E} = 600\ hr^{-1}$ ($0.17\ sec^{-1}$)

time of deformation = $t_d = 0.00267$ hr (9.61 sec)

time of cooling = $t_c = 0.0080$ hr (30 sec)

value of the constant C_o is $0.11°C^{-1}$. The temperature dependence of τ_{1s} and τ_{2s}, as given by equations (VI-31) and (VI-32), is plotted in Figure 16.

The theoretical stress at the end of the deformation may be obtained from equations (VI-21) through (VI-23) by setting $f(t) = 1$, $t_2 = t_c = 0$, $G_{ns} = G_{np}$, $\tau_{ns} = \tau_{np}$, and $t = 0$; this gives the following equation for the tensile stress at $t = 0$

$$\sigma_{11}(0) = \sum_n (A_n - B_n) = \sum_n G_{np}\left[\exp\left[- (1 - 2\dot{E}\tau_{np})\frac{t_d}{\tau_{np}} \right] - \exp\left[- (1 + \dot{E}\tau_{np}) \frac{t_d}{\tau_{np}} \right] + \frac{1 - \exp\left[- (1 - 2\dot{E}\tau_{np}) t_d/\tau_{np}\right]}{1 - 2\dot{E}\tau_{np}} - \frac{1 - \exp\left[- (1 + \dot{E}\tau_{np}) t_d/\tau_{np}\right]}{1 + \dot{E}\tau_{np}}\right] . \qquad \text{(VI-33)}$$

Using numerical values in Table II, equation (VI-33) may reasonably be approximated by

$$\sigma_{11}(0) = \sum_n G_{np}[\exp(2\dot{E}t_d) - \exp(- \dot{E}t_d)]$$

$$= \sum_n G_{np}\left[\left(\frac{L_g}{L_r}\right)^2 - \left(\frac{L_g}{L_r}\right)^{-1}\right] \qquad \text{(VI-34)}$$

which is the expected elastic result. Substituting numerical values into equation (VI-34) gives

$$\sigma_{11}(0) = 6.4 \times 10^7 \text{ dynes/cm}^2 \quad . \qquad \text{(VI-35)}$$

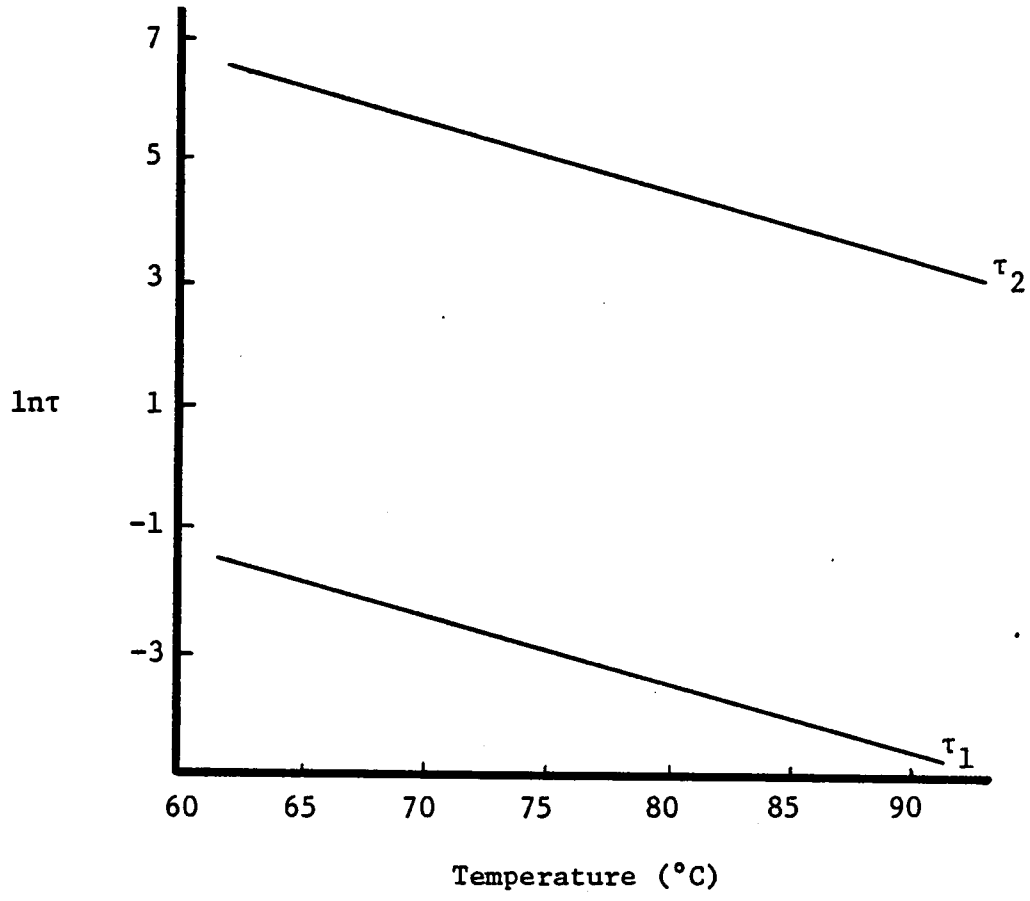


Figure 16. Temperature dependence of the relaxation times (in hours) used to fit the orientation aging data.

The experimental value for the stress after the deformation, obtained by Potnis (95) from birefringence measurements, is 5.6×10^7 dynes/cm^2. The discrepancy between the theoretical and experimental values is probably due largely to a slight error in the modulus.

The experimental data (obtained by Potnis (95)) and the theoretical curves (generated through a numerical solution of equation (VI-21)) are shown in Figures 17, 18, and 19. The curves are plotted as $f(t)(=L(t)/L_g)$ versus time. Figure 17 shows the results at 70°C; two cases were considered: (1) unloaded ($\sigma_o = 0$), and (2) 10 g load ($\sigma_o = 2.0 \times 10^7$ dynes/cm^2). Figure 17 shows that there is very little delayed deformation at 70°C; the temperature is apparently low enough so that the frozen orientation cannot appreciably relax. Figure 18 shows the results obtained at 80°C; three cases were considered: (1) unloaded ($\sigma_o = 0$), (2) 1 g load ($\sigma_o = 2.0 \times 10^6$ dynes/cm^2), and (3) 10 g load ($\sigma_o = 2.0 \times 10^7$ dynes/cm^2). There is significantly more delayed deformation at 80°C than at 70°C, but even at 80°C the samples do not approach their original rubbery length. The theoretical fits of the data are quite acceptable for all three cases; the theoretical effect of the 1 g load was somewhat underpredicted compared to the data. The results obtained at 90°C, shown in Figure 19, are obviously the most interesting because of the large observed effects. Again three cases were considered: (1) unloaded ($\sigma_o = 0$), (2) 1 g load ($\sigma_o = 2.0 \times 10^6$ dynes/cm^2), and (3) 10 g load ($\sigma_o = 2.0 \times 10^7$ dynes/cm^2). The theory and experiment are in good agreement for all three cases. The unloaded

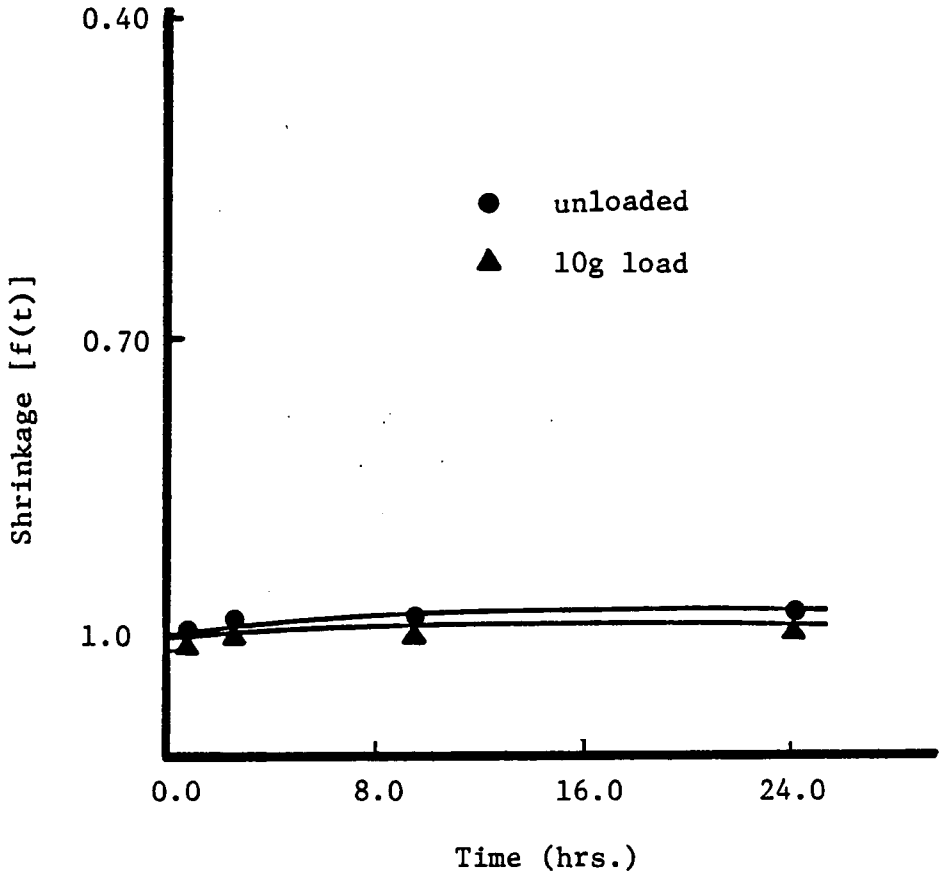


Figure 17. Theoretical fit of 70°C shrinkage data.

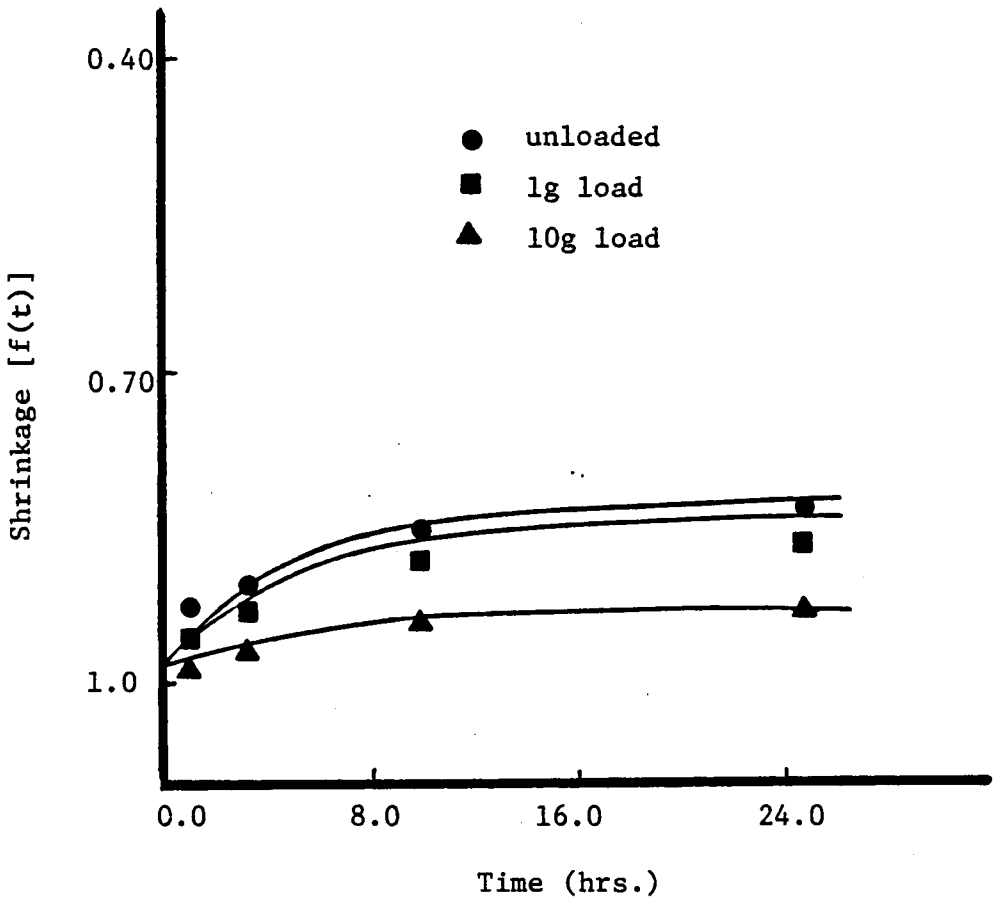


Figure 18. Theoretical fit of 80°C shrinkage data.

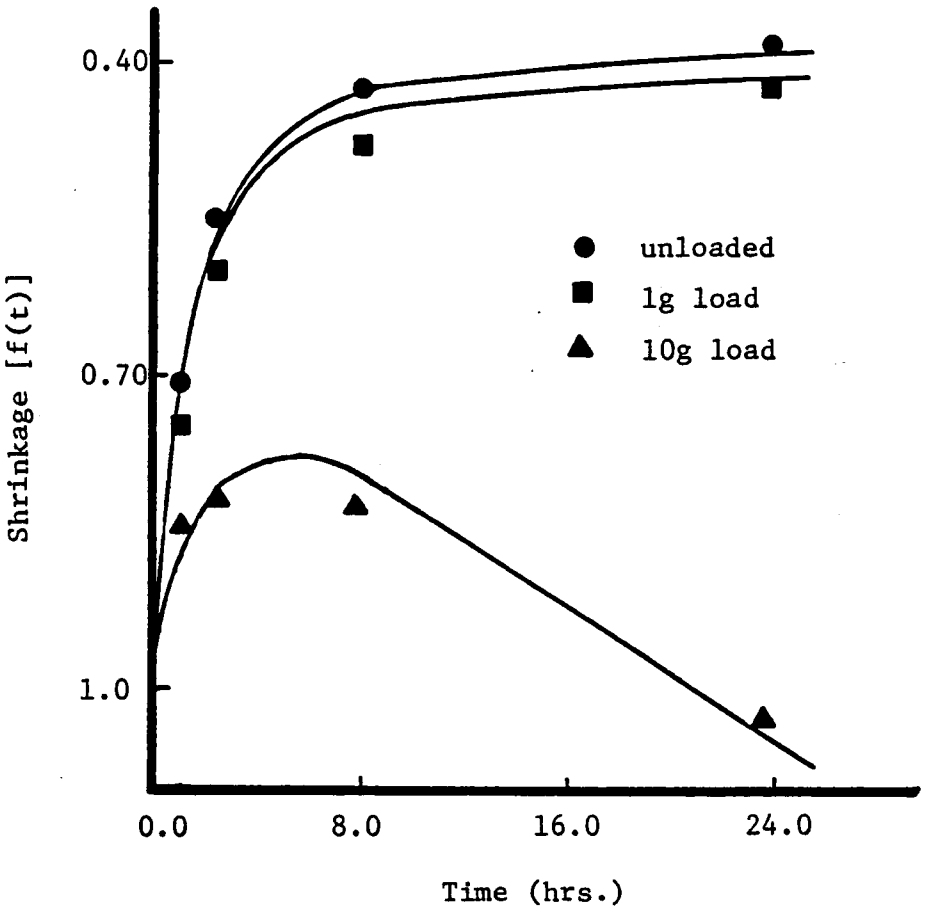


Figure 19. Theoretical fit of 90°C shrinkage data.

sample exhibited a considerable amount of elastic recovery; however, even at 90°C, it failed to return to the original rubbery length. Possibly the most interesting curve is the 10 g load. In this case the sample exhibits elastic recovery initially, but after about 6 - 8 hours creep begins to occur.

CHAPTER VII

SUMMARY OF IMPORTANT RESULTS

The work presented in this thesis is motivated by the desire to better understand the relationship between the rubbery and glassy states. The two phenomena studied in this work, which provide a connection between the two states, were free volume and molecular orientation. Both of these properties originate in the rubbery state and are frozen into the glassy state as the polymer is cooled through its glass transition. From a theoretical point of view, the rheological equations used in the two states are quite different. In the rubbery state a large deformation, time dependent, incompressible viscoelastic model is used; in the glassy state a small deformation, time independent, compressible elastic model is employed. Because many experiments of interest involve cooling through the glass transition, it would be useful to have a generalized model applicable in both the rubbery and glassy states. A specific form for such a model has been suggested.

Experimentally, the time dependent volume behavior of polystyrene was investigated. Volume aging studies were conducted at 90°C, 70°C, and 25°C. Attempts to construct a density gradient column operable at high temperatures were unsuccessful. The aging at 90°C and 70°C was carried out in a lab oven; the densities were measured by transferring samples from the oven to a density gradient column operating at room temperature. The aging densities and the

measured densities were assumed to be related with a glassy coefficient of expansion. This assumption is believed to be valid at 70°C but questionable at temperatures near 90°C. The aging data obtained at 90°C and 70°C indicates that the free volume decays quite rapidly in the first few hours (50-100 hours) of aging, but after the initial aging period the free volume decay becomes very slow. At 25°C the initial aging was considerably slower than at 90°C and 70°C, and even after 500 hours the free volume decay was still occurring at a measurable rate. Aging during the time the samples were settling in the density gradient column was also considered; a plotting procedure was suggested to correct for aging during settling.

A specific form has been proposed for a generalized integral constitutive model applicable either above or below the glass transition. The model is applicable to large deformations and it includes time effects and compressible effects. If the volume changes are set equal to zero, the model reduces to incompressible viscoelasticity; it reduces to classical linear elasticity for small strains, large time constants, and constant moduli. Also, if the stress has always been isotropic and the bulk modulus is assumed constant, a volume rate equation in differential form may be derived from the model.

The volume data was fit through a numerical solution of the previously mentioned rate equation. The functional form used for the relaxation time was modeled after the equations used by Kovacs.

An additional adjustable parameter, not present in the Kovacs equations, was required to fit the data. A single value of this parameter was sufficient to fit the 70°C and 25°C aging data; in order to fit the 90°C aging data, the parameter had to be changed. The rate equation was also used to determine the cooling rate dependence of the glass transition temperature; the theoretical predictions were in reasonable agreement with prior data obtained by Wust.

The incompressible form of the general integral model was used to fit orientation aging data obtained by Potnis. This required following the complete thermal and deformation history of the sample. The orientation induced through the deformation was frozen into the glassy sample as the material was cooled through its glass transition. The orientation decay was accompanied by a physical shrinkage of the sample; the shrinkage was obtained from the model by numerically solving an integral equation for the unknown deformation. The effect of an external load on the shrinkage was also considered. This analysis provided a good fit of the experimental data.

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APPENDICES

APPENDIX A

NOMENCLATURE LIST

A	cross-sectional area of sample
A_g	cross-sectional area of sample at end of deformation
A_n	defined by equation (VI-22)
a	density gradient column constant
a_T	temperature dependent shift factor
a_{TG}	temperature dependent glassy shift factor
a_{TR}	temperature dependent rubbery shift factor
a_{TV}	temperature and free volume dependent shift factor
a_{To}	temperature dependent shift factor used in orientation studies
a_V	free volume dependent shift factor
a_{VG}	free volume dependent glassy shift factor
a_{VR}	free volume dependent rubbery shift factor
B_n	defined by equation (VI-23)
b	density gradient column constant
C_n	defined by equation (VI-24)
C_o	defined by equation (VI-32)
C_T	defined by equation (V-10)
C_V	defined by equation (V-11)
C_1	WLF constant or constant in Mooney equation
C_2	WLF constant or constant in Mooney equation
c_{ij}	Cauchy strain tensor

c_{ij}^{-1}	Finger strain tensor
c_{ij}^{-1*}	normalized Finger strain tensor
c_{ijkm}	array of elastic constants
$\dot{E}$	deformation rate (defined by equation (VI-4))
F	load on sample
f(t)	deformation function (defined by equation (VI-7))
f_o	instantaneous deformation
G	modulus
G_p	modulus at the deformation temperature
G_s	modulus at the aging temperature
g	acceleration due to gravity
$H(\tau)$	continuous relaxation spectra
k	Boltzmann constant
L	sample length
L_g	sample length after deformation
L_r	sample length before deformation
m_1	memory function
m_2	memory function
N	number of polymer chains per unit volume
P	pressure
P_{ge}	equilibrium glass transition pressure
P_{ij}	extra stress associated with deformation
P_o	reference pressure
p	indeterminate scalar
R	cooling rate

R_p	radius of settling particle
T	temperature
T_{age}	temperature at which aging occurs
T_e	equivalent temperature
T_{ge}	equilibrium glass transition temperature
T_{meas}	temperature at which density is measured
T_o	reference temperature
T_r	reference temperature with respect to relaxation time
t	time
t'	past time (variable of integration)
t''	past time (variable of integration)
t_c	time of cooling
t_d	time of deformation
t_1	defined in kinematics (equation (VI-16))
t_2	defined in kinematics (equation (VI-17))
U	time dependent strain energy function or settling velocity
V	volume
V_o	reference volume
V_x	crosshead speed
v	specific volume
v_e	equilibrium volume (either v_r or v_g)
v_f	total free volume
v_{fe}	equilibrium free volume
v_{fn}	nonequilibrium free volume

v_g	glassy equilibrium volume (occupied volume)
v_o	reference specific volume
v_r	rubbery equilibrium volume
v_∞	equilibrium volume (Kovacs' notation)
W	strain energy function
w_{fc}	empirically introduced adjustable parameter
x	defined by equation (II-35)
Z	density gradient column reading
α	coefficient of expansion
α_r	rubbery coefficient of expansion
α_g	glassy coefficient of expansion
β	defined by equation (III-4)
$\dot{\gamma}_{ij}$	rate of strain
δ_{ij}	Kronecker delta
$\tilde{\varepsilon}_{ij}$	linear strain
θ	defined by equation (II-34)
κ_g	glassy compressibility
κ_r	rubbery compressibility
λ	Lamé's constant
λ^*	bulk modulus
μ	viscosity
ρ	density
ρ_{age}	density at aging temperature
ρ_f	fluid density
ρ_{meas}	measured density

ρ_o	initial density
ρ_∞	equilibrium density
σ_{ij}	stress
σ_o	defined by equation (VI-10)
τ	relaxation time
τ_G	glassy relaxation time
τ_R	rubbery relaxation time
τ_r	reference relaxation time
τ_{rG}	reference glassy relaxation time
τ_{rR}	reference rubbery relaxation time
τ_p	relaxation time at deformation temperature
τ_s	relaxation time at aging temperature
I,II,III	invariants of c_{ij}^{-1}

APPENDIX B

COMPUTER PROGRAMS

The computer programs used in the volume and the orientation studies are listed in this section. Program I was used for the volume studies; it solves the differential rate equation (equation (V-1)) for the volume as a function of time both during cooling and during the subsequent aging. Program II was used for the orientation studies; it solves the integral equation (equation (VI-21)) for the deformation f(t).

PROGRAM I

```
C THE FOLLOWING PROGRAM SOLVES THE DIFFERENTIAL RATE EQUATION FOR THE
C VOLUME AS A FUNCTION OF TIME BOTH DURING COOLING AND DURING THE
C SUBSEQUENT AGING -- THE EULER METHOD IS USED TO SOLVE THE DIFFERENTIAL
C EQUATION
C ----------
C ----------
C THE FOLLOWING FUNCTIONS DEFINE THE TEMPERATURE, TEM, AND EQUILIBRIUM
C VOLUME, VER FOR TEMPERATURES ABOVE TGE AND VEG FOR TEMPERATURES
C BELOW TGE
      TEM(X) = TC - R * X
      VER(X) = VO - ALR * (TC - TEM(X)) * VO
      VEG(X) = VO - ALR * (TO - TGE) * VC - ALG * (TGE - TEM(X)) * VO
C THE FOLLOWING FUNCTIONS ARE NEEDED FOR THE SHIFT FACTOR DURING
C COOLING
      WFR(Y,X) = Y - VER(X)
      WFG(Y,X) = Y - VEG(X)
      ATRR(X) = FDG * EXP(C1R * (TGE - TEM(X))/(TEM(X) - C2R))
      ATRG(X) = FDG * EXP(C1R * (TGE - TEM(X))/(TGE - C2R))
      ATGB(X) = EXP(CT * (TGE - TEM(X)))
      AVBR(Y,X) = EXP(-CV * (WFR(Y,X) - WFC)/WFG(Y,X))
      AVBG(Y,X) = EXP(-CV * (WFG(Y,X) - WFC)/WFG(Y,X))
      ATEFR(X) = ATRR(X) * ATGB(X)/(ATRR(X) + ATGB(X))
      ATEFG(X) = ATRG(X) * ATGB(X)/(ATRG(X) + ATGB(X))
      TAUFR(Y,X) = TAUC * ATEFR(X) * AVBR(Y,X)
      TAUFG(Y,X) = TAUC * ATEFG(X) * AVBG(Y,X)
C THE RIGHT SIDE OF THE DIFFERENTIAL EQUATION IS REPRESENTED BY THE
C FUNCTION FR(Y,X) OR FG(Y,X) -- IF THE TEMPERATURE IS ABOVE TGE THE
C FUNCTION FR IS CALLED AND IF THE TEMPERATURE IS BELOW TGE THE FUNCTION
C FG IS CALLED
      FR(Y,X) =  (VER(X) - Y)/TAUFR(Y,X) -  ALG * R * VO
      FG(Y,X) =  (VEG(X) - Y)/TAUFG(Y,X) -  ALG * R * VC
C THE FOLLOWING FUNCTIONS ARE NEEDED FOR THE SHIFT FACTOR DURING
C AGING -- THE TEMPERATURE IS CONSTANT DURING AGING
      WFA(Y) = Y - VEQ
      WFGA(Y) = Y - VEQG
      AVBA(Y) = EXP(-CV * (WFA(Y) - WFC)/WFGA(Y))
      TAUFRA(Y) = TAUO * AVBA(Y) * ATA
      TAUFGA(Y) = TAUO * AVBA(Y) * ATA
C THE RIGHT SIDE OF THE DIFFERENTIAL EQUATION IS REPRESENTED BY THE
C FUNCTION FRA OR FGA DEPENDING ON WHETHER THE TEMPERATURE IS ABOVE OR
C BELOW TGE -- DURING AGING THE COOLING RATE IS ZERO AND THE SECOND
C TERM ON THE RIGHT IS NOT PRESENT
      FRA(Y) =  (VEQ - Y)/TAUFRA(Y)
      FGA(Y) =  (VEQ - Y)/TAUFGA(Y)
C VALUES OF CONSTANTS
      TO = 118.0
      VC = 0.980
      TGE = 85.0
      ALR = 0.000370
      ALG = 0.000272
      DELAL = ALR - ALG
      R = 8.0
      C1R = 45.03
      C2R = 59.03
      CT = 1.0E-4
      TAUO = EXP(25.0)
      FDG = 1.0
C VALUES OF PARAMETERS -- IT IS NECESSARY TO CHANGE THESE VALUES
C DURING AGING
      CV = 15.0
```

PROGRAM I (cont'd)

```
      WFC = 0.0
C HEADINGS FOR OUTPUT
      WRITE(5,200)
       WRITE(24,200)
200   FORMAT(5X,'INCREMENT',5X,'TIME',5X,'TEMPERATURE',5X,'VOLUME',6X,
     1 'EQ.VOLUME',5X,'RELAXATION TIME')
C INITIALLY THE VOLUME IS VO
      V = VO
C THE STEP SIZE IS DELTI
      DELTI = 0.125
C IOUT IS A COUNTER USED FOR OUTPUT
      ICUT = 0
C START A LOOP OVER THE NUMBER OF INCREMENTS
      DO 99 INCRE = 1,93
C THE PRESENT TIME IS TIM
      TIM = INCRE * DELTI
C THE TEMPERATURE AT TIME TIM IS TEMP
      TEMP = TEM(TIM)
C THE TIME USED ON THE RIGHT SIDE OF THE EQUATION (TO CALCULATE THE
C VOLUME AT TIM) IS TIML
      TIML = (INCRE - 1) * DELTI
C THE VOLUME CORRESPONDING TO THE TIME, TIM, IS V -- THIS VOLUME IS
C EQUAL TO ITS PRIOR VALUE PLUS THE VALUE OF THE FUNCTION FR OR FG
C EVALUATED WITH THE PRIOR VALUE OF THE VOLUME AND TIME TIMES THE
C STEP SIZE -- IF THE TEMPERATURE IS LESS THAN TGE THE FUNCTION FG
C IS CALLED
      IF(TEMP.LT.TGE)GO TO 199
      V = V + FR(V,TIML) * DELTI
      GO TO 500
199   V = V + FG(V,TIML) * DELTI
      GO TO 510
C THE EQUILIBRIUM VOLUME AND EFFECTIVE TIME CONSTANT AT TIME TIM ARE
C COMPUTED FOR OUTPUT
500   VEQ = VER(TIM)
      TAUEF = TAUFR(V,TIM)
      GO TO 600
510   VEQ = VEG(TIM)
C IF THE SHIFT FACTOR BECOMES TOO LARGE AN OVERFLOW ERROR WILL RESULT
C AND THEREFORE AT TEMPERATURES LESS THAN 70 DEGREES THE VALUE OF ATRG
C IS TAKEN EQUAL TO ITS VALUE AT 70 DEGREES
      IF(TEMP.LT.70.0)FDG = ATRG(TIM)
      IF(TEMP.LT.70.0)CLR = 0.0
      TAUEF = TAUFG(V,TIM)
600   IOUT = ICUT + 1
      IF (IOUT.LT.1) GO TO 99
      IOUT = 0
      WRITE(5,100)INCRE,TIM,TEMP,V,VEQ,TAUEF
       WRITE(24,100) INCRE,TIM,TEMP,V,VEQ,TAUEF
100   FORMAT(5X,I5,4X,F10.3,4X,F10.4,1X,F12.6,4X,F10.6,5X,E12.5)
99    CONTINUE
C THE DENSITY AT THE END OF THE QUENCH IS COMPUTED FOR
C OUTPUT -- THIS DENSITY IS SHIFTED TO 23 DEGREES WITH
C A GLASSY COEFFICIENT OF EXPANSION
      V23 = V + ALG * (23.0 - TEMP) * VO
      DENSC = 1.0/V23
      WRITE(5,111)DENSC
       WRITE(24,111)DENSC
111   FORMAT(10X,'DENSITY AT 23 DEGREES =',1X,F9.6)
C THE AGING PORTION OF THE PROGRAM NOW BEGINS -- 'AGE' IS A PARAMETER
C INDICATING WHETHER OR NOT ANY AGING IS TO BE CALCULATED -- IF 'AGE'
```

PROGRAM I (cont'd)

```
C IS NEGATIVE NO AGING WILL BE CALCULATED
      AGE = -1.0
      IF(AGE.LT.0.0)GO TO 9999
C THE VALUES OF THE PARAMETERS CV AND WFC ARE ADJUSTED FOR AGING
      CV = 15.0
      WFC = 0.00090
C THE GLASSY EQUILIBRIUM VOLUME AND THE TEMPERATURE PART OF THE
C SHIFT FACTOR ARE COMPUTED FOR OUTPUT -- THESE QUANTITIES ARE
C CONSTANT DURING AGING
      VEQG = VEG(TIM)
      ATA = ATEFG(TIM)
      IF(TEMP.GT.TGE)ATA = ATEFR(TIM)
      WRITE(5,112)VEQG,ATA
       WRITE(24,112)VEQG,ATA
112   FORMAT(10X,'VEQG =',1X,F9.6,5X,'ATA =',1X,E12.5)
C HEADINGS FOR OUTPUT
      WRITE(5,950)
       WRITE(24,950)
950   FORMAT(5X,'INCREMENT',2X,'AGING TIME',3X,'TEMPERATURE',4X,
     1 'VOLUME',6X,'EQ.VOLUME',4X,'RELAXATION TIME',2X,'DENSITY, 23',
     1 2X,'REL.DENSITY')
C THE TEMPERATURE AT WHICH AGING IS OCCURING IS TAGE
      TAGE = TEMP
C THE STEP SIZE IS ADJUSTED FOR AGING -- FOR THE FIRST HOUR ONE
C SECOND STEPS ARE TAKEN
      DELTI = 1.0
C START A LOOP OVER THE NUMBER OF AGING INCREMENTS -- THIS FIRST LOOP
C WILL COVER THE FIRST HOUR OF AGING
      DO 299 INCREA = 1,3600
C THE AGING TIME IS TIMA
      TIMA = INCREA * DELTI
C THE VOLUME IS EQUAL TO ITS PRIOR VALUE PLUS THE VALUE OF THE FUNCTION
C FRA OR FGA EVALUATED WITH THE PRIOR VOLUME TIMES THE STEP SIZE --
C IF THE TEMPERATURE IS LESS THAN TGE THE FUNCTION FGA IS CALLED --
C THE EFFECTIVE TIME CONSTANT IS COMPUTED FOR OUTPUT
      IF(TAGE.LT.TGE)GO TO 350
      V = V + FRA(V) * DELTI
      TAUEF = TAUFRA(V)
      GO TO 360
350   V = V + FGA(V) * DELTI
      TAUEF = TAUFGA(V)
C THE AGING TIME IS CONVERTED TO HOURS FOR OUTPUTING
360   TIMHR = TIMA/3600.0
C THE DENSITY AT 23 DEGREES IS COMPUTED FOR OUTPUT
      V23 = V + ALG * (23.0 - TAGE) * VO
      DENS = 1.0/V23
C THE RELATIVE CHANGE IN DENSITY IS RD
      RD = (DENS - DENSO)/DENSC
      IOUT = ICUT + 1
      IF(INCREA.EQ.1)GO TO 774
      IF(ICUT.LT.60)GO TO 299
      ICUT = 0
774   WRITE(5,775)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
       WRITE(24,775)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
775   FORMAT(5X,I5,4X,F10.3,4X,F10.4,1X,F12.6,4X,F10.6,5X,E12.5,
     1 4X,F9.6,3X,E13.6)
299   CONTINUE
C THE STEP SIZE IS INCREASED TO ONE MINUTE
      DELTI = 60.0
C THIS LOOP COMPLETES THE FIRST DAY OF AGING
```

PROGRAM I (cont'd)

```
      DO 399 INCREA = 1,1380
C THE AGING TIME IS TIMA
      TIMA = 3600.0 + INCREA * DELTI
C THE VOLUME IS COMPUTED WITH THE SAME EQUATIONS AS BEFORE --
C THE EFFECTIVE TIME CONSTANT IS COMPUTED FOR OUTPUT
      IF(TAGE.LT.TGE)GO TO 450
      V = V + FRA(V) * DELTI
      TAUEF = TAUFRA(V)
      GO TO 460
450   V = V + FGA(V) * DELTI
      TAUEF = TAUFGA(V)
C THE AGING TIME IS CONVERTED TO HOURS FOR OUTPUTING
460   TIMHR = TIMA/3600.0
C THE DENSITY AT 23 DEGREES IS COMPUTED FOR OUTPUT
      V23 = V + ALG * (23.0 - TAGE) * VO
      DENS = 1.0/V23
C THE RELATIVE CHANGE IN DENSITY IS RD
      RD = (DENS - DENSO)/DENSO
      ICUT = ICUT + 1
      IF(ICUT.LT.60)GO TO 399
      ICUT = 0
      WRITE(5,875)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
       WRITE(24,875)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
875   FORMAT(5X,I5,4X,F10.3,4X,F10.4,1X,F12.6,4X,F10.6,5X,E12.5,
     1 4X,F9.6,3X,E13.6)
399   CONTINUE
C THE STEP SIZE IS INCREASED TO ONE HOUR
      DELTI = 3600.0
C THIS LOOP COMPLETES THE NEXT 29 DAYS OF AGING
      DO 499 INCREA = 1,696
C THE AGING TIME IS TIMA
      TIMA = 24.0 * 3600.0 + INCREA * DELTI
C THE VOLUME IS COMPUTED WITH THE SAME EQUATIONS AS BEFORE --
C THE EFFECTIVE TIME CONSTANT IS COMPUTED FOR OUTPUT
      IF(TAGE.LT.TGE)GO TO 550
      V = V + FRA(V) * DELTI
      TAUEF = TAUFRA(V)
      GO TO 560
550   V = V + FGA(V) * DELTI
      TAUEF = TAUFGA(V)
C THE AGING TIME IS CONVERTED TO HOURS FOR OUTPUTING
560   TIMHR = TIMA/3600.0
C THE DENSITY AT 23 DEGREES IS COMPUTED FOR OUTPUT
      V23 = V + ALG * (23.0 - TAGE) * VO
      DENS = 1.0/V23
      RD = (DENS - DENSO)/DENSO
      IOUT = ICUT + 1
      IF(ICUT.LT.10)GO TO 499
      IOUT = 0
      WRITE(5,975)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
       WRITE(24,975)INCREA,TIMHR,TAGE,V,VEQ,TAUEF,DENS,RD
975   FORMAT(5X,I5,4X,F10.3,4X,F10.4,1X,F12.6,4X,F10.6,5X,E12.5,
     1 4X,F9.6,3X,E13.6)
499   CONTINUE
C THE EQUILIBRIUM DENSITY IS COMPUTED FOR OUTPUT
      VEQ23 = VEQ + ALG * (23.0 - TAGE) * VO
      DENSEQ = 1.0/VEQ23
      WRITE(5,211)DENSEQ
       WRITE(24,211)DENSEQ
211   FORMAT(10X,'EQUILIBRIUM DENSITY AT 23 DEGREES =',1X,F9.6)

9999  STOP
      END
```

PROGRAM II

```
C THIS PROGRAM SOLVES AN INTEGRAL EQUATION FOR AN UNKNOWN DEFORMATION
C F AS A FUNCTION OF TIME -- THE MATERIAL IS AT REST FOR INFINITLY
C LONG TIME BEFORE BEING DEFORMED FOR A TIME TD -- AFTER THE
C DEFORMATION THE MATERIAL IS COOLED FOR A TIME TC -- AFTER COOLING
C THE UNKNOWN DEFORMATION OCCURS -- THE INTEGRALS ARE EVALUATED
C USING THE TRAPEZOIDAL RULE
C ----------
C ----------
C VALUES OF CONSTANTS
      G1R = 1.3E6
      G2R = 1.3E6
      G3R = 0.0E0
      G4R = 0.0E0
      G1P = G1R
      G2P = G2R
      G3P = G3R
      G4P = G4P
      G1A = 1.3E6
      G2A = 1.3E6
      G3A = 0.0E0
      G4A = 0.0E0
      G1S = G1A
      G2S = G2A
      G3S = G3A
      G4S = G4A
      T1P = 1.0
      T2P = 1.0
      T3P = 1.0
      T4P = 1.0
      T1A = 0.010
      T2A = 30.0
      T3A = 1.0
      T4A = 1.0
      T1S = T1A
      T2S = T2A
      T3S = T3A
      T4S = T4A
      EDOT = 600.0
      SIGO = 0.0
      TD = 0.00267
      TC = 0.0080
C VALUES OF PARAMETERS
      TC1 = TC/T1A
      TC2 = TC/T2A
      TC3 = TC/T3A
      TC4 = TC/T4A
      TD1 = TD/T1P
      TD2 = TD/T2P
      TD3 = TD/T3P
      TD4 = TD/T4P
      EDOTA1 = 1.0 - 2.0 * EDOT * T1P
      EDOTA2 = 1.0 - 2.0 * EDOT * T2P
      EDOTA3 = 1.0 - 2.0 * EDOT * T3P
      EDOTA4 = 1.0 - 2.0 * EDOT * T4P
      EDOTB1 = 1.0 + EDOT * T1P
      EDOTB2 = 1.0 + EDOT * T2P
      EDOTB3 = 1.0 + EDOT * T3P
      EDOTB4 = 1.0 + EDOT * T4P
      ASUB11 = G1R * EXP(-TC1) * EXP(-EDOTA1 * TD1)
      ASUB12 = G2R * EXP(-TC2) * EXP(-EDOTA2 * TD2)
```

PROGRAM II (cont'd)

```
      ASUB13 = G3R * EXP(-TC3) * EXP(-EDCTA3 * TD3)
      ASUB14 = G4R * EXP(-TC4) * EXP(-EDCTA4 * TD4)
      ASUB21 = G1P * EXP(-TC1) * (1.0 - EXP(-EDCTA1 * TD1))/EDCTA1
      ASUB22 = G2P * EXP(-TC2) * (1.0 - EXP(-EDCTA2 * TD2))/EDCTA2
      ASUB23 = G3P * EXP(-TC3) * (1.0 - EXP(-EDCTA3 * TD3))/EDCTA3
      ASUB24 = G4P * EXP(-TC4) * (1.0 - EXP(-EDCTA4 * TD4))/EDCTA4
      ASUB31 = G1A * (1.0 - EXP(-TC1))
      ASUB32 = G2A * (1.0 - EXP(-TC2))
      ASUB33 = G3A * (1.0 - EXP(-TC3))
      ASUB34 = G4A * (1.0 - EXP(-TC4))
      A1 = ASUB11 + ASUB21 + ASUB31
      A2 = ASUB12 + ASUB22 + ASUB32
      A3 = ASUB13 + ASUB23 + ASUB33
      A4 = ASUB14 + ASUB24 + ASUB34
      BSUB11 = G1R * EXP(-TC1) * EXP(-EDOTB1 * TD1)
      BSUB12 = G2R * EXP(-TC2) * EXP(-EDOTB2 * TD2)
      BSUB13 = G3R * EXP(-TC3) * EXP(-EDOTB3 * TD3)
      BSUB14 = G4R * EXP(-TC4) * EXP(-EDOTB4 * TD4)
      BSUB21 = G1P * EXP(-TC1) * (1.0 - EXP(-EDOTB1 * TD1))/EDOTB1
      BSUB22 = G2P * EXP(-TC2) * (1.0 - EXP(-EDOTB2 * TD2))/EDOTB2
      BSUB23 = G3P * EXP(-TC3) * (1.0 - EXP(-EDOTB3 * TD3))/EDOTB3
      BSUB24 = G4P * EXP(-TC4) * (1.0 - EXP(-EDOTB4 * TD4))/EDOTB4
      BSUB31 = G1A * (1.0 - EXP(-TC1))
      BSUB32 = G2A * (1.0 - EXP(-TC2))
      BSUB33 = G3A * (1.0 - EXP(-TC3))
      BSUB34 = G4A * (1.0 - EXP(-TC4))
      B1 = BSUB11 + BSUB21 + BSUB31
      B2 = BSUB12 + BSUB22 + BSUB32
      B3 = BSUB13 + BSUB23 + BSUB33
      B4 = BSUB14 + BSUB24 + BSUB34
      C1 = G1S/T1S
      C2 = G2S/T2S
      C3 = G3S/T3S
      C4 = G4S/T4S
C PRINT OUT VALUES OF THE PARAMETERS
      WRITE(5,175)A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4
      WRITE(24,175)A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4
175   FORMAT(5X,'A1 =',E12.5,1X,'A2 =',E12.5,1X,'A3 =',E12.5,1X,'A4 =',
     1 E12.5,1X,'B1 =',E12.5,1X,'B2 =',E12.5,1X,'B3 =',E12.5,1X,'B4 =',
     1 E12.5,1X,'C1 =',E12.5,1X,'C2 =',E12.5,1X,'C3 =',E12.5,1X,'C4 =',
     1 E12.5)
C THE INITIAL INSTANTANEOUS DEFORMATION IS FO - THIS IS SOLVED FOR
C IN THE SUBROUTINE INTOFM
      CALL INTOFM(FO,SIGO,A1,A2,A3,A4,B1,B2,B3,B4,ICOUNT)
C IF THE INITIAL DEFORMATION FO WAS NOT FOUND THE PROGRAM STOPS --
C (SEE THE SUBROUTINE INTOFM FOR EXPLANATION OF ICOUNT)
      IF(ICOUNT.GT.100)GO TO 9999
C THE INITIAL VALUES OF EACH OF THE INTEGRALS TO BE EVALUTED IN A
C SUBSEQUENT SUBROUTINE ARE ZERO
      SUM11 = 0.0
      SUM12 = 0.0
      SUM13 = 0.0
      SUM14 = 0.0
      SUM21 = 0.0
      SUM22 = 0.0
      SUM23 = 0.0
      SUM24 = 0.0
C THE STEP SIZE IS DELTI
      DELTI = 0.010
C THE PROCEDURE IS TO TAKE STEPS IN TIME SOLVING FOR THE VALUE OF THE
```

PROGRAM II (cont'd)

```
C DEFORMATION ON THE RIGHT HAND SIDE OF EACH INCREMENT - THE VALUE ON
C THE LEFT SIDE IS ALWAYS KNOWN - TO GET AN INITIAL GUESS IT WILL BE
C ASSUMED THAT THE VALUE ON THE RIGHT SIDE IS FR = SLP * TIMR + FO
C WHERE TIMR IS THE PRESENT VALUE OF THE TIME AND SLP IS AN EFFECTIVE
C SLOPE WHICH WILL BE ADJUSTED AFTER EACH CONVERGED VALUE FOR FR -
C INITIALLY THE VALUE ON THE LEFT SIDE (FL) IS EQUAL TO FO AND THE
C SLOPE WILL BE TAKEN AS ZERO
      FL = FO
      SLP = 0.0
C IOUT IS A COUNTER USED FOR OUTPUT
      IOUT = 0
C HEADINGS FOR OUTPUT
      WRITE(5,120)
      WRITE(24,120)
120   FORMAT(1X,'INCREMENT',2X,'TIME',4X,'DEFORMATION',7X,'ERROR',3X,
     1 'ITERATIONS',5X,'REL. DEFORM.',4X,'TIME.LT.0',6X,'TIME.GT.0')
C START A LOOP OVER THE TIME INCREMENTS
      DO 99 INCRE = 1,30
      IOUT = IOUT + 1
C ICOUNT IS A COUNTER ON THE NUMBER OF ITERATIONS REQUIRED TO REACH
C CONVERGENCE - IF ICOUNT EXCEEDS 100 THE PROGRAM STOPS
      ICOUNT = 1
C THE TIME ON THE LEFT SIDE OF EACH INCREMENT IS TIML AND ON THE RIGHT
C SIDE IS TIMR
      TIML = (INCRE - 1) * DELTI
      TIMR = INCRE * DELTI
C THE INITIAL GUESS AT F IS FR - THIS WILL BE ADJUSTED UNTIL IT
C CONVERGES
      FR = SLP * TIMR + FO
150   IF(ICOUNT.LE.100)GO TO 990
      WRITE(5,333)
      WRITE(24,333)
333   FORMAT(10X,'RUN DIVERGING')
      GO TO 9999
C THE INTEGRALS ARE EVALUATED IN THE SUBROUTINE SUMUP
990   CALL SUMUP(SUM11,SUM11D,SUM12,SUM12D,SUM13,SUM13D,SUM14,SUM14D,
     1 SUM21,SUM21D,SUM22,SUM22D,SUM23,SUM23D,SUM24,SUM24D,FR,FL,
     1 TIMR,TIML,T1S,T2S,T3S,T4S,DELTI)
C THE EQUATION IS REARRANGED TO A FORM SUITABLE FOR USING A SUCCESSIVE
C APPROXIMATION SCHEME TO ITERATE TO CONVERGENCE (HOPEFULLY) - THE
C EQUATION IS WRITTEN IN THE FORM
C          FR = (FUNCTION(FR,TIMR,INTEGRALS))**0.33333333
C FR IS USED TO COMPUTE A VALUE FOR THE RIGHT SIDE OF THE EQUATION
C WHICH IS CALLED FCHK - THE DIFFERENCE BETWEEN FCHK AND FR IS USED
C AS A CRITERION FOR HOW GOOD A GUESS FR WAS
      TRM1 = SIGO * FR**2.0
C IF X IS GREATER THAN ABOUT 80 THEN EXP(-X) WILL RESULT IN AN UNDERFLOW
C ERROR - THEREFORE IF TIMR/TIS IS GREATER THAN 80 IT IS SET EQUAL TO 80
      U1 = TIMR/T1S
      U2 = TIMR/T2S
      U3 = TIMR/T3S
      U4 = TIMR/T4S
      IF(U1.GT.80.0)U1 = 80.0
      IF(U2.GT.80.0)U2 = 80.0
      IF(U3.GT.80.0)U3 = 80.0
      IF(U4.GT.80.0)U4 = 80.0
      TRM2 = B1 * EXP(-U1) + B2 * EXP(-U2)
     1       + B3 * EXP(-U3) + B4 * EXP(-U4)
      TRM3 = C1 * SUM21 + C2 * SUM22 + C3 * SUM23 + C4 * SUM24
      TRM4 = A1 * EXP(-U1) + A2 * EXP(-U2)
```

PROGRAM II (cont'd)

```
     1        + A3 * EXP(-U3) + A4 * EXP(-U4)
         TRM5 = C1 * SUM11 + C2 * SUM12 + C3 * SUM13 + C4 * SUM14
         FCHK = ((TRM1 + TRM2 + TRM3)/(TRM4 + TRM5))**0.33333333
C THE QUANTITIES TLTO AND TGTO ARE (SOMEHOW) THE SUM TOTALS OF
C WHAT HAPPENED AT TIMES LESS THAN 0 (TLTO) AND TIMES GREATER
C THAN 0 (TGTO) - THEIR SUM SHOULD BE SIGO AND THIS IS USED AS
C A CHECK AS TO HOW GOOD THE CALCULATION IS
         TLTO = TRM4 * FR - TRM2/FR**2.0
         TGTO = TRM5 * FR - TRM3/FR**2.0
C THE ERROR AND ABSOLUTE VALUE OF THE ERROR ARE ERR AND AERR
         ERR = (FCHK - FR)
         AERR = ABS(ERR)
         IF(AERR.LT.1.0E-7)GO TO 200
C THE VALUE OF FR DID NOT CONVERGE AND THUS THE GUESS IS CHANGED AND
C THE ITERATION REPEATED
         FR = FR + 1.0 * ERR
         ICOUNT = ICOUNT + 1
C THE INTEGRALS ARE SET EQUAL TO THEIR PRIOR VALUES AND ANOTHER
C ITERATION IS EXECUTED
         SUM11 = SUM11D
         SUM12 = SUM12D
         SUM13 = SUM13D
         SUM14 = SUM14D
         SUM21 = SUM21D
         SUM22 = SUM22D
         SUM23 = SUM23D
         SUM24 = SUM24D
         GO TO 150
C THE VALUE OF FR HAS CONVERGED SO F IS SET EQUAL TO FR
200      F = FR
C THE RELATIVE DEFORMATION IS FREL AND IS GIVEN BY THE DEFORMATION
C DIVIDED BY THE INITIAL INSTANTANEOUS DEFORMATION
         FREL = F/FO
C THE LEFT HAND VALUE OF F IS SET EQUAL TO THE RIGHT HAND VALUE FOR
C THE NEXT STEP AND THE SLOPE IS CHANGED TO GET A NEW INITIAL GUESS
C FOR FR
         SLP = (FR - FO)/TIMR
         FL = FR
         IF(ICUT.LT.1)GO TO 99
         ICUT = 0
         WRITE(5,110)INCRE,TIMR,F,ERR,ICOUNT,FREL,TLTO,TGTO
         WRITE(24,110)INCRE,TIMR,F,ERR,ICOUNT,FREL,TLTO,TGTO
110      FORMAT(1X,I5,2X,F9.4,2X,E12.5,3X,E12.5,1X,I5,8X,E12.5,
     1 3X,E12.5,3X,E12.5)
99       CONTINUE
9999     STOP
         END
C ----------
C ----------
C THE SUBROUTINE INTDFM SOLVES FOR THE INITIAL DEFORMATION FO
         SUBROUTINE INTDFM(FO,SIGO,A1,A2,A3,A4,B1,B2,B3,B4,ICOUNT)
C IF THERE IS NO LOAD (SIGO = 0) THEN SOLVING FOR FO IS TRVIAL-
C IF THERE IS A LOAD AN ITERATIVE PROCEDURE IS USED TO GET FO --
C ICOUNT IS A COUNTER ON THE NUMBER OF ITERATIONS NEEDED TO REACH
C CONVERGENCE - IF IT EXCEEDS 100 "FO NOT FOUND" IS PRINTED AND
C CONTROL IS RETURNED TO THE MAIN PROGRAM
         ICOUNT = 1
         IF(SIGO.EQ.0.0)GO TO 500
C THE INITIAL GUESS AT FO IS FOGS
         FOGS = ((B1 + B2 + B3 + B4)/(A1 + A2 + A3 + A4))**0.3333333
```

PROGRAM II (cont'd)

```
535     IF(ICOUNT.LE.100)GO TO 515
        WRITE(5,533)
        WRITE(5,533)
533     FORMAT(10X,'FO NOT FOUND')
        GO TO 551
C THE EQUATION IS REARRANGED TO A FORM WHICH IS SUITABLE FOR USING
C A SUCCESIVE APPROXIMATION APPROACH TO ITERATE TO CONVERGENCE --
C THE GUESS FOGS IS USED TO COMPUTE THE VALUE OF THE RIGHT SIDE
C OF THE EQUATION WHICH IS CALLED FOCHK -- THE DIFFERENCE BETWEEN
C FOGS AND FOCHK IS USED AS A CRITERION AS TO HOW GOOD A GUESS
C FOGS WAS
515     SUMB = B1 + B2 + B3 + B4
        SUMA = A1 + A2 + A3 + A4
        FOCHK = ((SIGO * FOGS**2.0 + SUMB)/SUMA)**0.3333333
C THE ERROR AND ABSOLUTE VALUE OF THE ERROR ARE ERRO AND AERRO
        ERRO = (FOCHK - FOGS)
        AERRO = ABS(ERRO)
        IF(AERRO.LT.1.0E-4)GO TO 525
C THE VALUE OF FOGS IS CHANGED AND THE ITERATION IS REPEATED
        FOGS = FOCHK
        ICOUNT = ICOUNT + 1
        GO TO 535
525     FO = FOGS
        GO TO 510
500     FO = ((B1 + B2 + B3 + B4)/(A1 + A2 + A3 + A4))**0.3333333
510     WRITE(5,550)FO
        WRITE(24,550)FO
550     FORMAT(5X,'INITIAL DEFORMATION =',1X,E12.5)
551     RETURN
        END
C ----------
C ----------
C THE SUBROUTINE SUMUP EVALUATES THE INTEGRALS USING THE TRAPEZOIDAL
C RULE
        SUBROUTINE SUMUP(SUM11,SUM11D,SUM12,SUM12D,SUM13,SUM13D,
     1 SUM14,SUM14D,SUM21,SUM21D,SUM22,SUM22D,SUM23,SUM23D,SUM24,
     1 SUM24D,FR,FL,TIMR,TIML,T1S,T2S,T3S,T4S,DELTI)
C THE QUANTITIES SUMIJD ARE DUMMY VARIABLES - THE VALUE OF SUMIJD IS
C SET EQUAL TO SUMIJ AND THEN IF THE GUESS FR DOES NOT CONVERGE THE
C VALUE OF SUMIJ IS SET EQUAL TO SUMIJD FOR THE NEXT ITERATION
        SUM11D = SUM11
        SUM12D = SUM12
        SUM13D = SUM13
        SUM14D = SUM14
        SUM21D = SUM21
        SUM22D = SUM22
        SUM23D = SUM23
        SUM24D = SUM24
C EVAUATION OF THE INTEGRALS
        SUM11 = SUM11 * EXP(-DELTI/T1S) + (EXP(-DELTI/T1S) * FL**-2.0
     1          + FR**-2.0) * (DELTI/2.0)
        SUM12 = SUM12 * EXP(-DELTI/T2S) + (EXP(-DELTI/T2S) * FL**-2.0
     1          + FR**-2.0) * (DELTI/2.0)
        SUM13 = SUM13 * EXP(-DELTI/T3S) + (EXP(-DELTI/T3S) * FL**-2.0
     1          + FR**-2.0) * (DELTI/2.0)
        SUM14 = SUM14 * EXP(-DELTI/T4S) + (EXP(-DELTI/T4S) * FL**-2.0
     1          + FR**-2.0) * (DELTI/2.0)
        SUM21 = SUM21 * EXP(-DELTI/T1S) + (EXP(-DELTI/T1S) * FL
     1          + FR) * (DELTI/2.0)
        SUM22 = SUM22 * EXP(-DELTI/T2S) + (EXP(-DELTI/T2S) * FL
```

PROGRAM II (cont'd)

```
1         + FR) * (DELTI/2.0)
  SUM23 = SUM23 * EXP(-DELTI/T3S) + (EXP(-DELTI/T3S) * FL
1         + FR) * (CELTI/2.0)
  SUM24 = SUM24 * EXP(-DELTI/T4S) + (EXP(-DELTI/T4S) * FL
1         + FR) * (CELTI/2.0)
  RETURN
  END
```

VITA

Bradley D. Snow was born in Chattanooga, Tennessee on December 27, 1952. He graduated from Bartlett High School in 1970 and received the B.A. degree with a major in Criminal Justice from Memphis State University in December, 1975. In September, 1977 he entered The University of Tennessee Graduate School in the Department of Chemistry and received the M.S. degree with a major in Chemistry in June, 1981. In January, 1981 he entered the Polymer Engineering Department at The University of Tennessee and graduated with a M.S. in Polymer Engineering in March, 1983. On May 10, 1974 he married Debra Wallace of Forrest City, Arkansas. They have one child, Rachel, born on September 3, 1982.